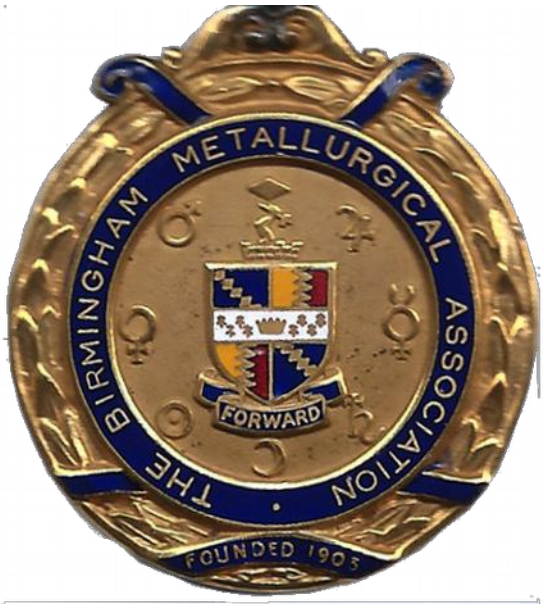
TITANIUM

by

W. J. KROLL

(A Lecture delivered to the Midland Metallurgical Societies, September 27th, 1954)



Transcribed from the Journal of the Birmingham Metallurgical Society,
(1954/5), XXXV, pp 248-302

EDITORIAL
THE KROLL PROCESS

These of us who were privileged to hear Dr. W.J. Kroll the inventor of the process for the reduction of titanium from its ores which bears his name, deliver the lecture on titanium which is published in this issue, came away with the impression that the occasion had been outstanding in the history of the Birmingham Metallurgical Society. In fact, it can be claimed that the occasion was unique in that as far as I am aware it was the first time that the Society had been had been addressed by a foreign scientist and certainly the first time it had listened to an inventor of a process of such metallurgical importance, describing his pioneer work

Born in Esch/Alzelte in Luxembourg in 1888, Dr, Kroll studied at the Technische Hochschule in Berlin-Charlottenburg, receiving his degree in 1918 after submitting a thesis on pure boron. After leaving the university, he specialized in the study of rare metals. Two industrial processes are based On Dr. Krolls early researches, the production of calcium-lead by reacting calcium carbide with lead, and the refining of bismuth-lead by calcium. In 1924 he founded his own laboratories in Luxembourg and remained there for sixteen years, Just before the last war Dr. Kroll went to the United States and became associated with the Union Carbide Research Laboratories at Niagara Falls. In 1945 he undertook research work on behalf of the U.S, Bureau of Mines in Albany, Oregon.

The name of Kroll is connected with a number of achievements in the field of metallurgy, Included among these are the fluoride reduction process for beryllium metal, and the production of hot malleable Manganese and chromium, but his main discoveries are concerned with the production of malleable titanium and zirconium, The basic idea underlying these processes was worked out as long ago as 1936, when he was in Luxembourg, but their application on an industrial scale did not take place until after he had joined the Bureau of Mines.

Despite all difficulties, and those that Dr. Kroll has had to face have been no mean ones, he has, with true scientific courage, persevered until his goal was reached, His singleness of purpose should be an example for us all and I am sure that the members the Birmingham Metallurgical Society will feel as honoured as I do that their Journal should be privileged to carry this record of an outstanding metallurgical development.

L.G. Beresford.

TITANIUM

by
W. J. KROLL
(Consulting Metallurgist, Corvallis, Oregon, U.S.A.)
(A Lecture delivered to the Midland Metallurgical Societies, September 27th, 1954)

It has been said that the birth of titanium was the greatest event in non-ferrous metals metallurgy since the introduction of the Hall-Héroult process of aluminium electrolysis. At present the total capital investment in the titanium industry may amount to 300 million dollars, and some people predict that it will ultimately reach the 10 billion dollar mark. This is advanced only to define the Importance of this subject.

Progress in developing titanium was not fast, however, until a few years ago, and the short historical review that follows shows that titanium has not been created by a single man, but by the exertions of many. More than a century ago, Berzelius[1] and his followers reduced potassium fluotitanate with potassium and obtained a blue metal powder that was heavily oxidized and nitrided. Nilson and Petterson[2] reduced, in 1887, titanium tetrachloride with sodium in a bomb and, probably because of a leakage, obtained only a nitrided powder metal. In 1910, Hunter[3] copied this method with more success since he obtained titanium granules which he described as hot malleable but brittle when cold. Nevertheless, Hunter may rightly be said to have been the first man who produced a somewhat ductile titanium,

Thanks to the pioneering work of Van Arkel and de Boer[4] who developed the famous iodide dissociation method, the first quantities of the pure element were made available, and its cold ductility was fully recognized, This refining method was not new in principle since it had already been proposed for the production of zirconium and tungsten by Weiss,[5] but the equipment devised by the Dutch scientists was so ingeniously conceived that up to now hardly anything better has been developed for the refine of raw sponge to a high purity metal. Going back to the reduction methods, Schubert and Schmidt[6] in 1892 reduced titanium tetra chloride with magnesium filings under carbon dioxide but they, of course, could not obtain anything but a black oxide powder.

The author's first experiments with the reduction of $TiCl_4$ under a noble gas, at substantially atmospheric pressure, in which double-distilled calcium was used as a reducing agent, were performed on June 17, 1937, and on June 30 of the same year a switch to the cheaper magnesium was made. This was preferred to sodium for other than price reasons. The author's idea of pressureless reaction was used at about the same time by Freudenberg,[7] who reduced $TiCl_4$ with sodium in a salt bath under hydrogen, which gas was, of course, not neutral to the titanium obtained. If Freudenberg had deoxidised carefully his KCl/NaCl flux, and if he had substituted argon for hydrogen as a neutral gas he would no doubt have obtained cold ductile titanium. The results of the author's experiments were published in 1940 and patents were obtained at about the same time.[8] A schematic drawing and a picture of the equipment used are shown in Figs. 1 and 2. The industrial counterpart can be seen in Fig. 3, which represents a 1,500 pound rector at Henderson, Nevada.

In 1939, while working with zirconium in Luxembourg we developed the vacuum separation of the magnesium chloride produced in the reduction. At the same time a change was made from vacuum sintering of the leached sponge turnings to von Bolton's arc melting[9] on a water-cooled copper plug which was seen in use at the plant of Siemens Halske. The author, however, worked with thoriated tungsten electrodes in a vacuum broken by a small amount of argon, and the furnace was all metal instead of glass. In 1938 almost all the present days alloys were being made and HF/HNO_3 solutions were introduced as an etchant to study the metallographic structure of titanium. In 1946, having developed the present day zirconium reduction process at the U.S. Bureau of Mines Station in Albany. Oregon, an arrangement was described[10] for industrial high temperature vacuum separation of the salts from the sponge, which was at once adopted by most of the American titanium producers.

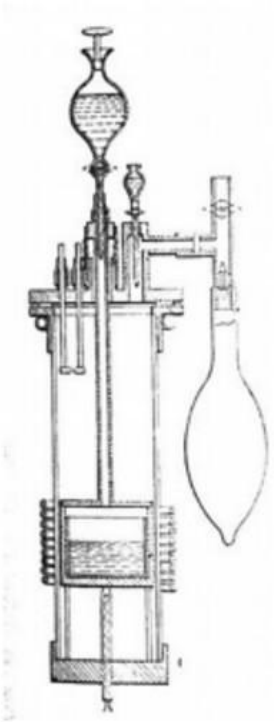


Fig. 1. Diagram showing the first laboratory Kroll reactor, according to U.S. patent 2,205,854, 1940

Fig. 2. View of reactor shown in Fig. 1. which produced the first titanium

Fig. 3. Large 1,500 lb. Reactor used at the titanium plant at Henderson Nevada.

In 1942 the U.S. Bureau of Mines in Boulder City, Nevada started work with the Kroll process on the basis of a vast project laid out by Dr. Reginald S. Dean, to investigate the possible uses of American ores. It is to the merit of Mr. F. S. Wartman, previously metallurgist at Boulder City, Nevada, to have industrialised the process, with the large means put at his disposal by the U.S. Federal Government. But even without this magnificent help the necessities of the atomic project would have independently started a titanium industry. The time was ripe for the birth of that metal with an almost unlimited ore basis.

The fate of great authors in finding their early manuscripts refused, and later recognised as masterpieces, was not spared the inventor of the magnesium reduction process, as appears from the fact that in 1938, on a trip to the United States, an attempt was made to sell the process to six of the first non-ferrous metal firms in that country, those efforts were ignored. What was worse, litigation had to be instituted against the U.S. Government for over five years, to get the seized patent rights back. The question of a refund of research investment and litigation expenses, fro royalties accruing, remains uncertain at the present time.

Before describing the main production process used industrially, a few salient facts of titanium chemistry and metallurgy will be glanced over. The difficulties encountered in reducing titanium to a ductile metal, result mainly from its high affinity for nitrogen and oxygen, and to some extent also from its multivalency. Since the aforesaid gases cannot be removed from contaminated metal by a high affinity scavenger, and since even melting *in vacuo* in presence of carbon does not deoxidise it, care must be taken not to bring it in contact with air constituents at elevated temperatures. This involves the use of a good vacuum or of a highly purified noble gas as a blanket, when heating the metal for a time above 800°C., and especially when melting it down. The multivalency causes the formation of low valency compounds with different physical properties and variable solubilities in fused carrier salts. This creates many difficulties in reduction processes and in the fusion electrolysis.

Ore Concentration

The main titanium ores available in quantity are rutile and ilmenite. The first is an oxide containing usually 95-98 Per cent TiO_2, the second an iron titanate with upwards of 32 per cent TiO_2, the balance being, besides iron oxide, CaO, MgO, MnO, Al_2O_3 and SiO_2, In 1953 the world supply of rutile reached 42,000 tons and most of it went into welding electrodes and in enamels, for which it is irreplaceable. On the other hand, the ilmenite supply, in the same year, was of the order of 800,000 tons, mostly were used in pigment and ferroalloy production.

While the supply of rutile is rather short and not indefinitely expansible, that of ilmenite within easy reach of transportation, is unlimited, the Canadian deposits at Allard Lake alone exceeding 300 million tons. It is evident, that if the new titanium metal industry has prospects of expanding to 100,000 tons/year, ilmenite is the only source of ore to be seriously considered as a raw material base. To use ilmenite however, presupposes that the problem of iron removal, by simple and cheap methods, can be solved. To use sulphuric acid for iron elimination is today a paying proposition for the production of expensive titanium oxide pigment, and, at the present high prices paid for titanium sponge, this method may even be considered temporarily for the production of a raw titanium oxide to be used for processing to the chloride and to the metal, because it permits short cutting the many chlorination difficulties resulting from the presence of impurities. However neither is the present pigment plant capacity available for this purpose nor could one think of dumping the enormous quantities of iron sulphate obtained as a waste, and there is no economical process available today that might permit recycling this sulphate to sulphuric acid and to produce a marketable iron oxide from it.

Direct chlorination of ilmenite produces iron trichloride besides $TiCl_4$. It would be impossible to dispose of the large quantities of $FeCl_3$ produced, despite the fact that there is a big market for it in sewage disposal. It would have to be processed in view of at least reclaiming its chlorine content,

but burning it up with oxygen, as has been suggested, awaits the solution of the many problems which this proposition raises.

The only iron separation process in view is the selective arc furnace reduction of the iron with production of semi-steel or cast iron besides that of a high titanium slag suitable for the chlorination. This suggestion is worth examining, It has been known for a century that a few percent of titanium oxide in the slag of a hot blast furnace causes difficulties with the fusibility. However, in a cold blast shaft furnace or cupola, easy running slags with 35 percent TiO_2 have been made when adding fluxes, In the arc furnace where higher temperatures can be obtained, less trouble is encountered with stiff slags, but fluxes have to be added if the ore itself does not contain enough fluxing constituents. This appears from the publications of Volkert,[11] Stoddard[12] and Knoerr.[13] The first of these proposed additions of lime/soda ash, which are both obnoxious if a chlorination is considered as the next step.

A systematic study of fusibilities and constitution diagrams of titanium slags by Sigurdson,[14] Armand[15] and Moore[16] has thrown some light on the problem, but unfortunately lower valency slags as produced industrially, have mostly been left out of consideration, as well as the possible formation of nitrides and carbides, which the iron metallurgist claims to be the main titanium slag stiffener.

These authors found the following lowest melting points in TiO_2 oxide mixtures: 1450°C. with 18 per cent CaO; 1705°C with 20 per cent Al_2O_3; 1606°C. with 8 per cent MgO and 1540°C with 20 per cent SiO_2. Alumina has been shown to be obnoxious in quantities above 10 per cent because it narrows the field of fluidity in ternary and quaternary systems. Silica would, to a large extent, be reduced to silicon, which would contaminate the iron and the part left in the slag would partially be chlorinated in the next step. The fluxing effect of CaO appears only when large amounts are added. The best choice of a flux is MgO, which may already be present in the ore in sufficiently large quantities to bring about fusibility.

Typical slags obtained in the operations at Sorel[13] contain for instance, 71.9 per cent TiO_2, besides 5.2 per cent MgO. Some ferrous oxide, 5-10 per cent, must be left behind in the slag to avoid formation of lower titanium oxides of reduced fusibility. Such slags have been tried in chlorination experiments, but it was found that the CaO and MgO form the respective chlorides, which impregnate the briquettes of the charge, film their surface and make the core less accessible to the chlorine.

Chloride residues. mixed with carbon and silica, pile up in the chlorinator, which must be cleaned from time to time. Exposure of the chlorinator walls to air causes moisture pick up and liberation of wet HCl, when starting the operation again. This may lead to heavy attack on the iron parts of the TCl_4 condensing system and plugs of hydrolyzed chlorides may form in the pipe lines. The volatile chlorides obtained besides $TiCl_4$ such as $AlCl_3$, and $FeCl_3$, are difficult to condense and their formation consumes chlorine. A 70 per cent titanium oxide slag needs an additional minimum, of 30 per cent chlorine beyond what is necessary for the chlorination of the titanium present, for the formation of parasitical chlorides of iron, calcium, magnesium, aluminium, manganese and silicon, which contaminate the batch in the form of oxides.

Some of the previously-mentioned difficulties with cleaning might be overcome by an airtight automatic mechanical removal of the residues from the chlorinator. The chlorine losses to the parasitical chlorides can be reduced by oxygen injection in the lower part of the chlorinator as suggested by the I.G. Farbenindustrie. The main effort is, at present, directed towards upgrading or elimination of slag constituents in the arc furnace at high temperature by volatilization, and toward using ilmenites with a low impurity content other than iron for the production of suitable slags. Simultaneously a slag, rich in TiO_2, is produced which disintegrates on cooling and which is quite exothermic on chlorinating. Since pure TiO_2 melts at 1840°C. and since no melting point below 1550°C. has been observed in the system titanium oxygen, the refractory problems facing the electro-metallurgist in slag upgrading are considerable. On the other hand the now available 70 per cent TiO, slags could also be processed, after iron separation by magnetic means, to carbide, whereby the CaO, MgO, part of the Al_2O_3 and SiO_2 could be volatilized, but a power consumption

of about 10kWh/kilo carbide could be expected in 1000 kW arc furnace units for this operation. The chlorination of this product could be greatly simplified, since a water-cooled iron shell could be used in which the self sustaining reaction with chlorine proceeds.

The iron winning side in the arc furnacing of ilmenite is not brilliant. The iron obtained, which is a semi-steel or pig-iron, contains most of the sulphur of the ore, usually upwards 0:5 percent, which is costly to remove. It 1s quite probable that present attempts at concentrating the TiO_2 content in slags beyond 70 per cent will result in the creation of products that can compete with commercial grades of rutile as a feed for chlorinators.

Chlorination

Relatively little has been published about the chlorination of rutile or slags, except in a Fiat Report on pre-war German practice.[17] In general the titanium-bearing material is ground to 200 mesh, mixed with ground charcoal or petrol coke and pitch, briquetted and baked at temperatures of 500 – 800°C. The Henderson, Nevada plant[18] of the Titanium Metals Corporation does not briquette, but pours the paste mixture on a rotating hearth which passes through a brick-firing kiln. Conditions in baking are critical for the next step, that of chlorination. If the baking temperature is not high enough, residual hydrogen originating mostly from the pitch brings about the formation of excessive quantities of HCl in the chlorination, which, besides causing chlorine losses, create also a disposal problem of HCl. Usually the batch is charged medium hot, but in the chlorinator, especially if no extra heating means are provided.

The IGFarbenindustrie[17] add some excess carbon and use oxygen to maintain the heat balance of their unheated chlorinator. The usual chlorinators for magnesium chloride production[19] can be employed, which provide for internal heating with electricity passed through graphite bricks. This gives more suppleness when starting and during the operation. No information is available as yet as to current experiments with chlorination in a fluidised bed.

The chemistry within the chlorinator is rather complex. The carbon added to the batch should, for reasons of economy, produce in preference CO_2, while the titanium liberated in the reduction should combine with the chlorine present to form anhydrous $TiCl_4$. In reality CO also forms besides CO_2 and the operation, when adding a large excess of carbon can even be directed so as to yield mostly CO besides chlorine. The height of the batch has some bearing as to the CO_2/CO ratio obtained since the carbon present is a reducing agent for the carbon dioxide. The temperature at which the chlorination takes place also has its bearing on the CO_2/CO ratio, a high temperature favouring the production of monoxide. A chlorination with exclusive CO_2 formation liberates three times more heat than if CO alone was produced. Free CO may combine with excess chlorine to form $COCl_2$, at medium temperature. This gas in itself a powerful chlorinating agent and as such it may penetrate the batch and contribute largely to chlorination and reduction

It is evident that the chlorination by such a gaseous reducing agent is more efficient than that by a solid carbon and chlorine mixture, since the latter relies entirely on a carbon contact for its success. However, phosgene is increasingly dissociated above 560°C, so that its action is limited to the upper and cooler section of the batch. Naturally free CO may also act as an independent and penetrating reducing reagent, and the iron liberated by reduction may then react quite easily with any free chlorine present. There is also a more universal interchlorination and interreduction of the compounds contained in the batch or formed from it. It is known, for instance, that $TiCl_4$, is a good chlorinating agent for Fe_2O_3[20] and the oxygen of the iron is switched to the titanium whereby, in equilibrium reaction, $FeCl_2$ is liberated. $SiCl_4$ is quite as efficient for the chlorination and reduction of metal oxides as is $TiCl_4$[21]. Also TiO_2 may lose some oxygen above 1200°C., by dissociation or reduction, which temperature may be reached locally, and the lower titanium oxide so produced is capable of reacting back with iron oxide, forming TiO_2 again and liberating iron.

Silica, if present as such, is hardly attacked by carbon and chlorine below 1000°C,, but any silica tied up in double compounds, such as aluminates is chlorinated together with the other oxide partner. Alumina is mostly chlorinated and volatilized as chloride. The oxides of manganese, calcium and magnesium are easily chlorinated by chlorine in presence of a reducing agent, thus

causing losses of the halogen. In this respect the presence of hydrogen in the batch is much more detrimental because of the low atomic weight of this element which ties up 35 times its own weight of chlorine. All these reactions are temperature dependent.

The condensing system behind the chlorinator is usually provided first with a hot cyclone dust chamber, in which flue dust is deposited, followed by a condenser chamber for the iron chloride, held at about 220°C. A silica brick-lined iron tower filled with porcelain pebbles is used next to condense $TiCl_4$ and residual $AlCl_3$ and $FeCl_2$. It is sprinkled internally with raw, cool $TiCl_4$ which is drained from the bottom tank and passes through a heat exchanger. This method of condensing $TiCl_4$ is subject to patents of the Pittsburgh Plate Glass Company.[22] The bottom tank collects a finely-divided aluminium chloride and iron chloride as sludge, which can be decanted or filtered and separated by distillation of the $TiCl_4$ contained, The raw $TiCl_4$, before being fractionated is treated with either copper powder, hydrogen sulphide or vegetable oils to remove vanadium, probably present as $VOCl_3$ by reduction to less volatile and insoluble compounds which can be decanted, The two first methods of vanadium elimination are described in a report of the U.S. Bureau of Mines.[23]

$SiCl_4$ 57-.7°C.; Si_2Cl_6 139.0°C.; $COCl_2$ 8.3°C.;
$VOCl_3$ 126.7°C.; Si_2OCl_6 137-138°C.; Cl_2 -33.7°C.;
HCl 83.7°C.

Fractional distillation permits separation of $TiCl_4$ from $SiCl_4$. However, some probably oxidized chlorinated silicon compounds of a boiling point close to that of $TiCl_4$ (B.P. 136.4°C) can interfere with the purification. Such products, if present in the purified chloride may later increase the hardness of the metal produced therefrom because they introduce oxygen. The main impurities that can be contained in the raw chloride and their boiling points are:are: Continuous rectification with Dowtherm as a heat control medium is now being generally adopted, Pure $TiCl_4$ is rather expensive to produce and, at a price of $4.50/lb. Of titanium sponge it represents at its market price 59 per cent of the total cost of metal production. The titanium in the a ilmenite, for comparison, amounts only to 1.6 cts/lb of contained metal. Improvements in the production of cheaper purified $TiCl_4$ are at present, much more interesting, than changes in the reduction methods In view of lowering the price of sponge

Reduction and Purification

Having described how the starting materials usable for the reduction to metal can be made, namely the oxide and the anhydrous chloride, the possible or proposed titanium reduction and purification processes will now be examined before the standard industrial method of magnesium reduction of the chloride is described.

Titanium oxide can be reduced to a rather pure sponge with distilled calcium as a reducing agent, Kubaschewski[24] has shown that an oxygen content as low as 0.07 per cent is thus obtainable, which would be equivalent to the one of metal reduced from the chloride. According to some patents of the Dominion Magnesium Company[25] the reduction could be performed in two steps, first with magnesium, followed by acid extraction of the MgO produced and then with pure calcium which would only be used for a thorough after-reduction. This, of course, would greatly cheapen the process. Up to now, calcium reduced titanium metal with a hardness better than 220 Brinell has not appeared in the market. An analysis of such metal given recently by Rylski[26] shows the following per cent impurities of such titanium:

O_2 0.47; N_2 0.16; H_2 0.017; C 0.25

The carbon content is avoidable and the nitrogen could probably be lowered by using a better grade calcium. The difficulties with calcium reduction reside in the equilibrium:

$$TiO_2 + 2Ca \leftrightarrow 2CaO + Ti.$$

High temperatures and low pressure shift the reaction to the left, as can be seen from the fact that *in vacuo* calcium metal is obtained from a CaO/Ti mixture, and this even much easier than from a CaO/Si batch, which latter is recommended for calcium production. This means that for a complete

reduction of TiO_2 one has to operate at low temperature and at as high a pressure as possible. One has also to create large contact surfaces, eliminate CaO as it is formed, and use a considerable excess of calcium. At the most suitable temperatures of 850-1200°C and at atmospheric pressure, a complete reduction is not accomplished, at least not with large batches. Sintering of the titanium particles may be responsible for the incomplete reduction. The calcium used must be free of nitrogen, which latter hardens about 2½ times faster than oxygen. Fine calcium turnings, when exposed to the air pick up nitrogen, which adds to the difficulties.

Among the many titanium production processes which have been tried and abandoned are those involving hydrogen as a reducing agent for the halogenides. The bromide reduction on a hot filament has been used in Germany by the Osram Company[7] with some success. High power consumption, lower titanium bromide by-products , and the necessity for reclaiming HBr formed are serious objections to this method, which also requires very pure hydrogen. The reduction of the chlorides in an arc with hydrogen once suggested by Jaffee[27] has not been mentioned again. Arc reduction presupposes, among other things. That the electrode problem can be solved. A high amperage arc is out of the question since even with cooled carbon or tungsten electrodes a reaction with the titanium produced must be expected at the the hot tips. A high voltage arc would permit using cool electrodes. But this raises all the problems of the Birkeland-Eyde nitrogen oxidation process. The reclaiming of by-product HCl, and of lower titanium chlorides, constitutes in itself a series of operations for which economical solutions have not been found as yet. Continuous removal of the hot titanium produced would prove to be a most difficult task on account of its sticky properties.

Hydrogen reduction is also frequently a part of the disproportioning methods recommended for titanium production, in so far as hydrogen may be used to produce $TiCl_3$ from $TiCl_4$. It is rather easy to produce $TiCl_3$ by reduction of $TiCl_4$ with aluminium according to Ruff.[28] The $AICl_3$ by-product has a market value, but it does not have unlimited sales prospects. The reduction of $TiCl_4$ to $TiCl_3$ with hydrogen is not easy because of a simultaneous partial breakdown to $TiCl_2$, which latter is said to be pyrophoric. Also the reduction has to take place 1300 – 1400°C, which creates almost insurmountable refractory problems. The recoveries do not exceed 70 per cent. In the subsequent disproportionating of $TiCl_2$ at lower temperatures according to $2TiCl_2 \leftrightarrow Ti + TiCl_4$ only part of the titanium is reclaimed, this being in powder form, and the $TiCl_4$ by-product must be recycled. It is to be hoped that experience acquired with the much easier production of aluminium by way of AlCl made from $AlCl_3$ and scrap metal, which is now being tested on a pilot plant scale, might bring some prospect for the titanium lower chloride disproportionating. The necessity of recycling the HCl by-product remains as a problematic sideline of this method. For the treatment of titanium scrap by passing $TiCl_4$ over the latter and producing $TiCl_2$, the disproportionating method may offer some possibilities if the refractory problem can be solved, the more so since in this case no HCl by-product is obtained.

Fluoride Reduction

Anhydrous TiF_4, sublimes at 284°C.[29] and melts at 400°C. Under pressure, which makes it quite similar as to its physical properties to anhydrous zirconium chloride. This would suggest that the method now used for the production of zirconium from its gaseous chloride might also be adaptable to titanium fluoride, but in this case magnesium cannot be used as a reducing agent since the MgF_2 formed melts at 1300°C., at which temperature titanium would strongly react with the iron vessel used. Also the fluoride produced cannot be separated from the sponge by leaching with water because of its insolubility in this medium, Replacing magnesium with sodium, whose fluoride is soluble in water, could not be recommended, either, if the zirconium reduction technique was used, because the sodium fluoride obtained melts at 997°C., at more than 100°C, above the boiling point of the element. It might, however, be possible to react TiF_4 with sodium at medium temperatures, for instance S00°C, ie, much below the melting point of sodium fluoride, when using a mixer to break up the NaF cake, as recommended in a recent patent for the production of titanium from its chloride with sodium as a reagent.[30]

On the other hand, one could think of reducing a mixture of sublimed TiF_4 powder and magnesium chips in a pressure vessel at a high enough temperature to melt the MgF_2 obtained (M.P, 1300°C.) in a flash, or, better, to melt also the titanium produced (M.P, 1660°C.) and to bring about a clean separation of metal and slag. This would be feasible only if a suitable lining for the bomb could be found, which would not introduce oxide in the metal produced. The use of a pressure vessel puts serious limitations on this process with regard to the size of the equipment, which must be small because of the high pressure produced by the titanium fluoride and the magnesium gas, partially heated to the melting point of titanium.

It is said that anhdyrous titanium fluoride is quite inert in air and insensitive to water,[29] which would be a definite advantage in its handling. It can be produced from anhydrous HF and TiO_2, but sulphuric acid besides CaF_2 is needed for the production of HF, and it is wasted as calcium or magnesium sulphate, if in the latter case the magnesium fluoride obtained in the reduction was recycled for recovery of its fluorine content. Since fluorine is 3.2 times more expensive than chlorine on an equivalent basis, it is doubtful whether it could compete with the latter even with the recycling scheme mentioned. At present the cost of chlorine in anhydrous $TiCl_4$ amounts 11.2cts/lb. of titanium produced, not considering the losses if the magnesium chloride produced is not recycled for chlorine and magnesium and, as can be deduced therefrom, the use of fluorine would cause an extra expense of 24½ cts/lb. of titanium produced. This would not appear worthwhile if no special advantages could be derived from this method.

The reduction of the alkali fluorotitanates with sodium usually leads to a very impure, oxide bearing titanium powder. The main reason is hat these salts are usually slightly hydrolysed and they oxidise when drying. Oxygen from the air does not displace fluorine from these salts[31] when hot, but HF is formed moisture and fluorides which can be oxidised with water at medium temperature. If the double fluorides are thoroughly deoxidised before use, for instance by passing HF_2, CCl_2F_2 or NH_4F over or through them, complete deoxidation can be obtained.

It is questionable whether, even with a fully deoxidised fluorotitanate, an oxide free titanium could be produced, since in the presence of alkali fluoride the reduction yields a powder, which is depassivated by fluorides and liable to be oxidised by water in the subsequent leaching operation. Sodium must be used as a reducing agent since magnesium or calcium would raise the melting point of the batch too much by formation of the rather difficult to fuse fluorides. These cannot be leached with water. Finally there is the question of the production of low cost fluorotitanate. It can be obtained only by attack of ilmenite by hydrofluoric acid, the fluoride of which latter, is per equivalent, as shown above, much more expensive than chlorine. While the alkali fluoride could be recycled with sulphuric acid to reclaim its fluorine content as HF, the reducing agent itself, namely sodium, is not recoverable in this operation.

Iodide Titanium

The iodide dissociation process might be turned from a purification into an extraction method by bleeding purified gaseous titanium iodide into a dissociator provided with a hot target.[32] This is being attempted by the Battelle Memorial Institute for the Kennecott Copper Company. The iodide cannot be obtained directly from the carbide iodisation except at very high temperatures where the lower iodides are formed, which are not usable as such.[33] Normally the tetraiodide from aluminium titanide by reaction of iodine within a solvent, the former attacking both constituents of the alloy.[34] Separation of the attacking AlI_3 produced is obtained by fractional distillation. Recuperation of iodine from this by-product creates a special problem. The continuous removal of he hot titanium target grown over with titanium crystals, from the high vacuum room to the air is not easy. The power consumption of the freely radiating target must be high. Iodine losses at $2.50/lb are of serious Consequences, especially when considering, the high atomic weight of this element which requires moving 10lb, of iodine for each lb. of titanium produced.

Fusion Electrolysis

Great effort has been concentrated on this method, up to now with rather poor success, The reasons for this are many, They have been discussed in detail elsewhere.[35] In the fusion electrolysis of titanium one must consider the following requirements: A suitable electrolyte; its thermal stability, its behaviour to the cell liner; its necessary oxide content to avoid anode effect with graphite anodes; the necessity of internal heating of the cell by direct passage of the current; the cell construction with regard to the aggressive products liberated at the anode; arrangements to keep the cathodes under argon protection after lifting them out of the bath until they cool down for removal through gates to the atmosphere; methods for introducing fresh electrolyte of definite oxide content in the cell; mechanical devices within the cell to move and replace cathodes and to provide for their rapid connection with the bus bars.

The choice of suitable electrolytes is limited for price reasons to fluorides and chlorides, Pure titanium fluoride (B.P, 284°C. M.P. about 400 C, under pressure) cannot be used as an electrolyte because of its physical properties, but the double fluorides of titanium with potassium, sodium and lithium, could be considered. These can be obtained from aqueous solutions. They have, according to Ginsberg[36] the following melting points: $2NaF,TiF_4$ 700ºC., $KF.TiF_4$ 780ºC., LiF,TiF_4 450ºC. All these salts dissociate in alkali fluoride and TiF_4 below their melting point. It is therefore probable that none of these complexes exists in the fused state. It is common practice to lower the melting points of double fluorides in view of obtaining a stabler bath and for this purpose alkali chlorides are usually added. A typical case is the one of sodium chloride additions to the cryolite bath which has been discussed by Haber.[37] Horizons[38] propose the addition of alkali chlorides to fluorotitanates. In any such electrolyte chlorine is developed at the anode, if enough chloride is present, because free fluorine, as evolved anodically reacts with alkali chloride with liberation of chlorine according to a well known reaction used for the determination of free fluorine.[39] Therefore, the Horizons bath behave almost entirely like a chlorine electrolyte. This type of operation will be examined further.

Next to the lack of stability of the fluoride bath, the necessity of adding oxide to avoid anode effect with graphite anodes must be stressed. No fusion electrolysis whether chloride or fluoride, according to experiments made by von Wartenberg,[40] can be operated successfully with graphite or carbon anodes if the bath not contain oxide. This is, for instance, a well known and essential requirement in the aluminium electrolysis of cryolite, it has been found necessary in any fluoride electrolysis such as those of Ta, U, Be, Zr and Ce. The anode effect is, for the main part caused by a halogen or halogenide gas skin adherent to the graphite, which stops the flow of the current. There are also some other reasons for this phenomenon, but this is the main one. This gas skin can be broken down if CO_2/CO is developed simultaneously at the anode, which is the case when sufficient oxide is present in the bath to react with the free halogen and the carbon with the formation of carbon oxides besides the respective halogen compounds, which latter dissolve in the bath.

While the fluoride electrolysis requires the presence of considerable quantities of oxide in the electrolyte, which is decomposed by the current and from which the metal is deposited exclusively, much less is needed in the chloride electrolysis. Furthermore, in the fluoride bath no fluorine is developed at the anode except when anode effect takes place, in which case it is converted to carbon tetrafluoride, which may be the main gas coating the anode. It is found in the waste gases when this phenomenon occurs. In the chloride electrolysis on the contrary, chlorine is liberated at the anode because only these are decomposed by the current and also very small, but essential, quantities of CO_2/CO are formed by anodic reaction of dissolved oxides with carbon. This shows that the carbon anode plays an important role insofar as it continuously deoxidizes the electrolyte up to the point when oxide must be added to avoid anode effect. Therefore, the question may be asked where the oxide comes from in a plain chloride electrolyte of an operating cell to which only “ anhydrous” chlorides are added.

There are two sources of oxide, which are usually overlooked when running a chloride electrolyte; moisture and oxygen from the air. At the bath surface moisture reacts to an equilibrium with the fused chlorides liberating HCl and forming oxides, which dissolve in the electrolyte, Furthermore, there is, to a lesser degree, a direct substitution of chlorine in the hot chlorides for

oxygen of the air at the bath surface, also to an equilibrium point. These oxides too go into solution. Fluorides are not oxidized by oxygen,[31] though easily by moisture. This all shows what happens when the bath surface is sealed off from the air, for instance with a blanket of noble gas, as is done in titanium electrolysis. Since the anode deoxidises the electrolyte continuously, while in this case no oxide is introduced by reaction with the air, the bath, after a while suffocates for want of oxygen and anode effect takes place. This is frequently overlooked since the blanketed cell may be fed with already oxidized or moisture-bearing fresh electrolyte, thus getting the oxide it needs, and, in order to maintain a sealed cell in operation, it must be fed with an oxide-bearing electrolyte. Since oxygen in some form, must be dissolved in the bath to maintain the operation, it can be expected that it will take part in contaminating the dendritic titanium deposit.

Excessive amounts of oxide must be avoided, but what is the limit in view of getting around the anode effect and of obtaining a soft low oxide metal? Nothing is known about that for the chloride electrolyte but it is certainly necessary to add prohibitively large amounts of oxide to a fluoride bath, the oxide being the only compound taking part in this electrolysis. This practically rules out any fluoride electrolysis with graphite anodes on account of the contamination of the titanium crystals by dissolved oxide.

The chloride electrolyte must evidently be conditioned as to the right amount of oxide to produce a low oxygen titanium. This can be done by running the cell for a while so that the carbon of the together with the halogen liberated at its surface can deoxidise to the desired degree. On the other hand one can deoxidise also by chemical means, for instance by blowing into the electrolyte reagents that halogenize and deoxidize as well, such as HCl, CCl_4 or $CHCl_3$. Such reagents are used today in a similar case for the deoxidation of barium chloride steel hardening baths.

The oxide present in a chloride bath has some other side effect, as, for instance, the one of bringing about a dissolution of titanium. Gill[41] has shown, that titanium metal dissolves in fused chlorides, but in presence of air only, forming hydrosols, and the bath obtained plates out titanium alloy in contact with copper or iron, possibly from a divalent state. The chemistry of this phenomenon is not known.

As mentioned above, the addition of sufficient alkali chloride to a fluorotitanate bath converts the latter into a pseudo chloride electrolyte, which yields chlorine at the anode and only little oxide has to be present to avoid anode effect. Such a bath as suggested by Horizons[38] can, however, not be kept in operation for a long time because, since fluorotitanate and alkali chloride are being added while titanium and chlorine are withdrawn, alkali fluoride evidently accumulates in the cell. The fluorotitanate is the source of the titanium deposited and it is decomposed by the alkali metal produced at the cathode. Its price has a decisive effect on the cost of operation of this process.

A general drawback of the titanium electrolysis, which shows how vain is any attempt at lowering the melting point by adding some other alkalis, appears from observations made by Andrieux.[42] and Drossbach,[43] The former has shown that titanium ions do not take part in the electrolysis, that the reduction takes place in valency steps and by alkali or alkaline earth metal reaction with the titanium halogenide at the cathode. This confirms some observations of Andrieux with similar electrolytes, which showed the reaction products, namely the halides of these metals accumulate and freeze at the cathode to form a solid “boule.” For instance, in a fluoride bath the dendrites deposited may be in a solid, difficultly fusible matrix of NaF (M.P. 997°C.) which progressively blocks the passage of current. These salts should redissolve in the fused electrolyte which usually has a lower melting point but, since their formation is local and much faster than their diffusion, solid accretions form on the cathode whereby the bath composition changes by progressive elimination of one of the constituents. To avoid this the cell must be run hot enough and preferably at a temperature exceeding the melting point of any of the components of the bath, This shows that attempts at lowering the melting point of an electrolyte may defeat themselves by the chemistry of the cell.

Some observations have already been made about the chloride electrolyte as far as a comparison with the fluorides was needed. Usually a chloride electrolyte is made up of a titanium chloride dissolved in a carrier salt. At present our knowledge about the solubility of titanium

chlorides in other fused chlorides is very poor. It is said that complexes $TiC1_4$,LiCl and $TiCl_4$.KCl can be melted at temperatures below 450°C.[44] and that the electrolysis can be performed with these at this low temperature. They dissociate above 500°C. However. the multivalency of titanium has to be considered, too, since $TiCl_4$ breaks down at the cathode to trivalent and divalent forms,which results in higher melting points at least at the cathode, the readily fusible tetravalent complex being destroyed. $TiCl_4$ is not soluble appreciably at atmospheric pressure in fused NaCl, $CaCl_2$, $MgCl_2$,, $BaCl_2$ or $SrCl_2$ nor in any carrier salt at temperatures in excess of 500°C. This rules out the use of $TiCl_4$ as a bath constituent in any fusion electrolysis above that temperature.

On the other hand the work of Cordner[45] has demonstrated that the lower titanium chlorides $TiCl_3$ and $TiCl_2$ are soluble in various carrier salts and that suitable electrolytes can be obtained with these. Lower titanium chlorides having to be used, means for preparing them have to be foreseen. usually for this purpose $TiCl_4$ is bubbled into the fused electrolyte in a non-compartmented cell, together with hydrogen as a reducing agent. Under such conditions the chlorine evolved at the anode combines with the hydrogen which must be in a large excess to allow also for the reduction of $TiCl_4$ to the lower valency chlorides, to be dissolved in the bath. The hydrogen reduction of the tetrachloride creates problem of the regeneration of waste HCl formed, which has already been mentioned.

The lower valency electrolyte is naturally chlorinated by the chlorine of the anode and the $TiCl_4$ produced there, not being soluble in carrier salt, escapes with the chlorine and must be reclaimed from the waste gases. On the other hand, titanium dichloride is produced at the cathode from any trichloride present in the electrolyte by reaction with the titanium dendrites, which lowers the current efficiency. Any tri- or dichloride of titanium entrapped in the titanium crystal is lost by hydrolysis in the following leaching step, by which the dendrites are reclaimed. If a diaphragm could be found to separate the anodic and cathodic bath, the difficulty resulting from the anodic destruction of the lower valency chlorides could be avoided, but the hope of finding a material of construction, pervious to the electric current, resistant to the aggressive action of strongly reducing electrolytes at a temperature of at least 800°C., is dim. All that can be hoped for is to be capable of building a dam perhaps water cooled, across the cell to separate anode and cathode rooms below and above the bath, the dam dipping a few inches into the electrolyte. This principle of the dam is applied in magnesium cells. A separation of anode and cathode room above the bath is necessary to collect the chlorine and to protect the titanium and the hot iron parts of the cathode from an attack by this gas. The cathode room is therefore also usually filled with argon.

The cell constructions proposed for the electro-winning of titanium are, as far as they are divulged in the literature nothing but enlarged laboratory units, in which none of the above-mentioned requirements of construction have been taken care of. Usually the cell body is drilled out of a graphite electrode, which is a financially ruinous proposition. Also, such graphite body is not leak proof as to the salts it has to contain, The cells are not compartmented,which gives the chlorine free access to hot iron parts constituting the cathode. On cathode removal, argon is admitted intermittently, which leads to a waste of noble gas. The cathodes are changed only after shutting down the current, a method that can be used only when a cell is heated externally. This is not practicable for any industrial cell. No suggestion has been made as to automatic lifting of loaded cathodes from the bath, for their replacement by fresh ones, nor has any mechanism been described that would permit removal of the pyrophoric cathodes to a cool room and thence through gates to the atmosphere. Losses of titanium crystals to the bottom of the cell always occur. Hard accretions form with these and the capacity of the cell is gradually decreased. While ;one Can hope that some of these difficulties will be overcome, the fusion electrolysis is still in the far future for titanium winning.

Shawinigan Water & Power[46] proposed to use the sodium sued in a Downs cell *in situ* to reduce $TiCl_4$, which is instilled into the cathode compartment at a rate providing for a slight excess of sodium. It is already difficult to operate a Downs cell for sodium alone, and to try to remove simultaneously the titanium sponge produced without interruption would add unbearable complications. Excessive heat evolution in the cathode room can be counted on and the metal

obtained is certainly harder than the one made directly with purified oxide-free sodium, since the electrolyte entrapped in the sponge contains oxide as described above. The continuous withdrawal of titanium from a normal reactor is still an unsolved problem and to perform similar operation with a sodium cell must be quite troublesome.

The substitution of fusion electrolysis for magnesium or sodium reduction is not as promising from the economic angle as is generally claimed. The power consumption is expected to be small for the direct electrolysis of titanium, which is an advantage only in countries with high power cost. Supposing that for the production of one pound of titanium by magnesium reduction one would need twice the amount of electrical energy required for the production of one pound of magnesium, this would still not represent more than 4 per cent of the present market value of titanium at the present day power prices in the U.S.A., as against almost 60% per cent for the chloride, which is needed as raw material in the fusion electrolysis as well as in the reduction. Savings that could be made in the continuous leaching of the cathode deposit are shared in the sodium reduction of $TiCl_4$ since the sponge produced that way can be leached. Titanium losses in the electrolysis are certainly higher than in metal reductions because of the hydrolysis of the titanium salts, entrapped in the crystals.

Soluble Anode

Fusion electrolysis with a titanium anode has better prospects. Starting, for instance from scrap titanium, cast in the form of anode plates, one can, with a bath containing lower titanium chloride, dissolve titanium anodically and transfer it to the cathode, where it is deposited in the form of dendrites. The anode is fully depolarized, the bath needs no oxide and no anode effect can interfere. The electrolyte must naturally be protected from oxidation by the air by a noble gas blanket, but no separation of anode and cathode compartments is necessary since no chlorine is evolved at the anode, which simplifies the construction. However the electrolyte being of lower valency, probably mostly divalent, the titanium chlorides entrapped in the crystals are lost by hydrolysis on leaching. This loss can be minimised by using an electrolyte with a low titanium content. The voltage in such a cell being low, since the current is not used for any chemical work, it might be difficult to keep the bath hot by the passage of direct current alone.

The first interest in such an arrangement is the refining action that is expected to take place, Nitrogen and carbon are eliminated as such, which is a positive asset of this process. Nothing is known definitely as to the behaviour of small amounts of oxide. Larger quantities are certainly carried over from the anode to the cathode, and TiO anodes, as proposed in one patent[47] do sot produce an oxide free cathode deposit. Some oxide dissolved in the bath can be reduced by extraneous means, for instance by blowing HC] gas into or around the anode, or by using for this purpose mixtures of $TiCl_4$ and hydrogen, which liberate HCl, but this method is rather ineffective. Very soft titanium crystals have been obtained with the soluble anode, which indicates that an unknown mechanism of deoxidation is at work, at least in a chloride bath, provided the quantities of oxide present in the anode metal are small. The carbon contained in the anode material or introduced in the casting procedure may be a contributing factor in the deoxidation. Perhaps there might also be a question of lack of solubility of lower oxides in the chlorides.

The refining electrolyte being one of lower titanium valency, the less electropositive metals that might go into solution at the anode as chlorides, are reduced by the bath according to the following equation:

$$2TiCl_2 + FeCl_2 \leftrightarrow 2TiCl_3 + Fe$$

These metals go into the sludge as such, This reaction depletes the electrolyte of divalent titanium and the bath must recondition itself to the divalent form by the reaction of the trichloride with the anode titanium or with cathode dendrites if one does not assist it with other reducing agents.

The purification with regard to less electropositive impurities than titanium by the soluble anode method is here possible only because of the formation of lower valency titanium salts. Metals that have only one valency, such as manganese, do not allow such purification if used as anodes

since the less electropositive impurities, once they are dissolved in the bath as chlorides, cannot in this case be reduced in any way by a valency change reaction[48] of manganese.

It is probable that impurities that form highly volatile chlorides, such as silicon, sulphur and phosphorus, will be eliminated by volatilisation at the titanium anode, provided their solubility in the bath at the given temperature is low.[49]

Before this refining method could be made commercial for scrap refining, thought would have to be given to some of the problems of cathode removal without losing any deposit, in absence of air by continuously-operating mechanical devices, without interrupting the current. The elimination of sludge, the reclaiming of hydrolyzed titanium salts from the leaching liquors of the cathode, the reduction of the volume of salts entrapped in the crystals by squeezing the hot cathodes as indicated elsewhere for the iron powder electrolysis[48] would have to be the subject of extended research. After it has been found that a cell of simple construction with a soluble anode can be operated reliably for scrap purification, the problem of running the complex one with graphite anodes for direct metal winning can be approached with more confidence.

Commercial Production

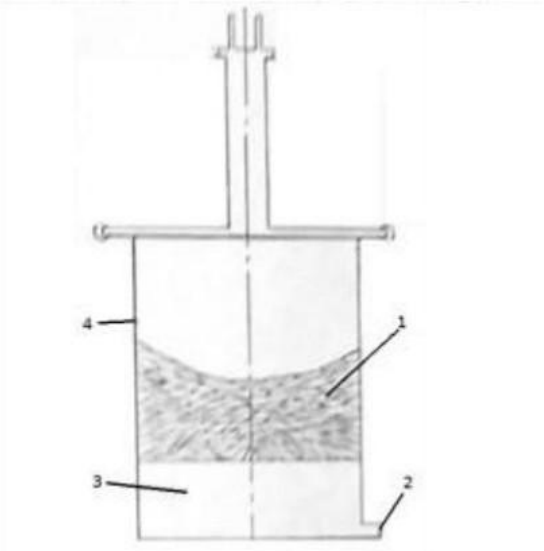
The only process used at present industrially for the production of titanium starts with tetrachloride, which is reduced under a noble gas, at substantially atmospheric pressure with a reducing agent having a sufficiently high chlorine affinity, The question whether to substitute sodium for magnesium as a reducing reagent will be discussed later,

Magnesium reduction will be examined first. A recommended procedure is to melt all the magnesium needed for the reduction plus a 15 per cent excess, under argon or helium, and to drip $TiCl_4$ on the bath at a temperature not exceeding 950°C, because otherwise iron might be picked up from the reactor. The argon acts as a regulator for the speed of the reaction, if used with care, especially in case of a runaway, It also prevents air from leaking back in the apparatus if a slight positive gas pressure is maintained. The titanium chloride may also be introduced as a gas, which method is, however, more complicated and introduces more heat in the system. The volume of the $MgCl_2$ produced being about 10 times that of the sponge obtained, it is evident that this salt must be drained or tapped repeatedly in the course of the reduction. This can be done by releasing it either inside the reactor or outside to the atmosphere. The latter practice is more common. The risk of having air drawn back into the equipment at that moment can be minimised by maintaining a slightly higher argon pressure in the reactor during tapping.

Wartman[49] recently examined the conditions under which the reduction takes place. He found that no reaction occurs below the surface of the fused magnesium when all the magnesium needed is present at the start of the run, and that sponge formation begins at the iron wall of the reactor, just at the circular zone of the magnesium level, as indicated in Fig 4 The sponge growth is horizontal inwards from the wall and vertical upwards in the right angle between bath level and crucible wall. It is maintained exclusively by capillarity or wick action of the sponge and of the iron wall, which are wetted by the fused magnesium After a while bridging of the sponge takes place in the middle of the crucible and the downward flow of the fused MgCl, formed may then be impeded. The space taken up by the fused magnesium fills up progressively with salt which pushes residual magnesium upwards into the sponge. After about 40 per cent of the magnesium has been reacted the remainder is entirely absorbed by capillarity on the surface of the sponge, The consequence is that the space occupied by the fused magnesium at the beginning of of a run is not being used for sponge growth if the vault formed is not knocked down.

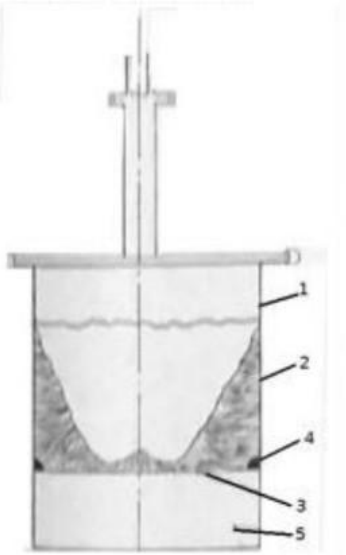
For fuller use of the capacity of the crucible, one could think of not introducing the reducing agent at once at the beginning but of adding it at intervals in small portions in function of the needs of the reaction. In this way a kind of a sponge layer cake could be built, while the salts could be drained continuously. However, when considering the problem of the impurities of the magnesium, this proposition has some drawbacks. If all the magnesium needed is admitted in the beginning, the first titanium produced will getter the noble gas atmosphere, forming titanium oxide and nitride,

either directly or by way of magnesium oxide and nitride obtained by the gettering action of the magnesium.



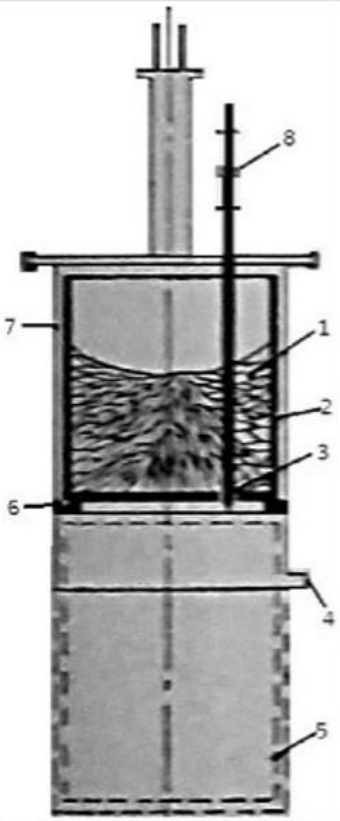
1 – Reactor 2 – Sponge 3 – Bridge 4-Spot where reaction starts. 5 – Space taken originally by fused magnesium

Fig. 4. Cut through a reactor after 40% of the theoretical amount of magnesium has reacted. All residual magnesium is impregnated in the sponge. After F.S. Wartmen



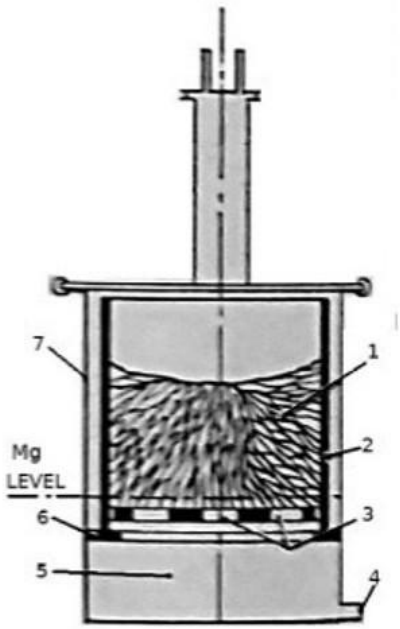
1 – Sponge 2 -Taphole 3 – Space taken originally by the fused magnesium. 4 – Reactor wall.

Fig. 5. Wartman reactor.



1 - Sponge. 2 – Insert crucible. 3 – Tapping rod and hole 4 – Outside tapping hole. 5 – Salt can. 6 -Supporting flange. 7 – Reactor wall. 8 – Vacuum joint.

Fig. 6. Reactor with crucible insert and tapping rig either to tap salts and collect them in a can inside or to tap them from a forehearth a second time outside. Dotted lines represent tapping inside the ractor



1 – Sponge. 2 – Insert crucible. 3 – Holes in crucible bottom. 4 – Taphole. 5 – Space taken originally by magnesium used as a forehearth. 6 – Supporting flange. 7 – Reactor wall

Fig. 7. Reactor with crucible insert. Automatic salt draining into forehearth through perforated bottom. Tapping to the air by separate taphole.

Furthermore, a great many impurities contained in the magnesium are tied up with the first titanium produced, which acts as a scavenger for the reducing agent forming the titanides of Si, Al, Fe, Ni, Cu, and Mn.

These impurities are deposited in a definite sponge zone, namely at the iron wall and at its junction with the magnesium bath's level where the reaction starts. They can be eliminated mechanically in later processing of the sponge, of which certain sections, especially of the centre, are of extreme purity. Evidently the impurities of the magnesium are spread all over the titanium batch if the reducing agent is added in small quantities as needed. Gettering of the argon within the reactor at the start and purifying the molten magnesium separately before it is used, for instance by a preliminary reaction with some $TiCl_4$ might be resorted to in order to avoid the disadvantages when feeding small quantities of the metallic reactant but this adds to the complications. Feeding the reaction with liquid magnesium as needed leads to the production of a dense sponge, which releases its chloride content during the vacuum distillation only with difficulty. Also, repeated liquid feeding causes some trouble in so far as the magnesium reacts at the inlet with the $TiCl_4$ that is present in the argon atmosphere, and forms accretions which after a while plug up the hole.

A question of importance resulting from the growth of the sponge on the iron wall is the one, whether an insert crucible should be used from which the sponge could be recovered by mechanical means, or whether one should let the sponge deposit on the reactor wall, from which it could be removed by turning it out on a lathe. Since a suitable set-up also depends on the needs for tapping the salt, some possible solutions have been shown in Figs. 5-7.

The arrangement of F. S. Wartman in which the sponge grows directly on the reactor walls, is shown in Fig. 5. It is turned out after the reaction on a lathe in an air-conditioned room. The salts are tapped out to the air during the reduction, which entails some risk of air leaks into the reactor, The disposition of Fig. 6 shows the use of a crucible inserted in the reactor shell. It is provided with a mechanical tapping device that permits emptying the salts in a can arranged in the lower section of the vessel, The can may also be omitted, in which case the salts may be tapped or drained into an anteroom and from there subsequently to the air. Fig. 7. shows an insert crucible with a perforated bottom arranged within the reactor shell on a flange, at a certain level above the bottom. The magnesium level must evidently be maintained in the beginning of the run above the perforated plate on which the sponge then grows in preference to the walls, while the salts collect below the crucible in the forehearth. From there they can be tapped periodically to the atmosphere. Collecting all the salts of one operation in a can within the reactor shell leads to large vessels considering the great volume of the salts produced. However, this way of proceeding has the advantage of avoiding air leaks that may happen when tapping the salts to the atmosphere

A crucible insert has some disadvantages as, for instance, the smaller capacity compared with that of the reactor itself and the gap which it creates between the crucible wall and the reactor vessel. This gas space makes heat dissipation more difficult. Usually, when growing the sponge on a reactor wall, the reaction product is turned out in a dry room on a horizontal lathe. Such a room represents some quite heavy capital expenditure, and the heavy lathe is also costly. The humidity of this room must be held below ½ per cent. In the case of leaching the turnings, dry room separation is still required, only far the purpose of leaving in the crucible a protecting layer of reacted material for the next run, which reduces iron contamination, Tile layer should, of course, remain dry.

When operating with an insert one generally does not turn out the reaction product, but one processes the whole crucible with the reacted mixture in a vacuum retort at high temperate, where the salts are distilled off. The sponge obtained in this operation becomes coalesced and sinters very tight. It is much less pyrophoric than the sponge as reduced, is gas free, but sticks tight to the iron wall, from which it is quite difficult to remove, even with compressed air chisels. Attempts at lining the crucible with high carbon steels or with chromium iron alloy sheets which stick much less, met with some success, Naturally, the part of the sponge in contact with the iron can be expected to be contaminated somewhat, but it is common practice to run the reduction when using a crucible insert at a much lower rate and consequently lower temperature than when growing it on the reactor wall, because of the heat dissipation problem in the first case and the greater risk of serious iron

contamination. Thus the iron pick-up is reduced at the expense of an extended reaction time at a lower temperature. If a perforated crucible is used, as shown in Fig. 7, care must be taken that at the beginning the magnesium level is held slightly above the perforated bottoms plate. Also the insert crucible must fit tightly on its support so that no magnesium can leak into the space between insert and reactor wall which otherwise would fill up with the sponge, and would make the removal quite difficult.

After draining the magnesium chloride the sponge is still impregnated with 10 to 15 per cent of the salt and it contains besides this, the magnesium excess of about 15% needed for the reduction. With less than 10 per cent magnesium excess purple titanium trichloride appears in the salt. This chloride also shows up when running the reaction too fast. To obtain a magnesium and chloride free sponge two ways are open, leaching or vacuum distillation at elevated temperature. Both methods are practise. The drawbacks oft leaching are many. First hydrochloric acid must be used to extract large amounts of magnesium which are lost in the dilute chloride solution: Titanium Metals Corp[19] use this procedure and an inhibitor is added to the acid. Naturally, the impregnated magnesium chloride also goes to waste in the aqueous solution besides the one produced from magnesium with the acid, while the vacuum distillation permits reclaiming both the magnesium and the anhydrous salt, besides eliminating hydrogen.

The production of turnings suitable for the leaching as to size brings about a problem of oversize chips. These must be ground under adverse conditions in presence of $MgCl_2$, which is slippery and acts like a lubricant. There being a danger of explosion if the atmosphere above the leaching tanks contains more than 4 per cent hydrogen, these become very bulky on account of the necessary slow feeding rates. In the leaching the sponge is unavoidably loaded up with hydrogen, which, if high, must be removed by vacuum annealing before arc melting. The sponge not being sintered, as compared with the one obtained in the high temperature vacuum salt distillation process, its activity is greater and some reaction with water might be expected. This results presumably in a higher percentage of fines and in a raised oxygen content of the chips but no data as to recovery in function of hardness is available.

Such leaching permits producing a sponge with less than 0.1 per cent chlorine but 0-3 per cent Mg usually remains behind, this being apparently the limit of solubility of magnesium in titanium. The fines contain more iron than the dense sponge and with their removal the iron content of the output is lowered, The depreciated fines can be used for the production of titanium master alloys which are in demand by steel mills because of their low carbon, silicon and aluminium content. However, the titanium in such alloys cannot be marketed at a higher price than $2.60/Ib. of titanium contained. One definite advantage of the leaching is that it can be performed mechanically in a continuous operation and in standard equipment, at low cost.

In the high temperature vacuum separation of the $MgCl_2$ and excess magnesium a titanium recovery of 95 per cent of the batch with a maximum hardness of 180 Brinell can be obtained. This method has, however, some disadvantages. The retorts shown in Fig. 8 have to be supplied with a vacuum equipment which is expensive in maintenance. One has to operate in batches and the present size of the retort is limited to about 2 tons input. The cycle is slow, especially with larger batches because of the difficulty of heat dissipation after the run, The energy consumption is rather high since the heat accumulated in the iron parts of the retort is lost on cooling, but the one contained in the brick work of the electric vacuum furnace can be reclaimed in the next run. The excellent quality obtained in vacuum distilled metal appears from the the fact that Japanese sponge with a hardness below 130 Brinell, is being offered in quantity. The chlorine and magnesium content can be held below 0.15 and 0.1 per cent respectively. Better results as to these impurities may be obtained with turnings made from the batch in a dry room and submitting these to the vacuum process.

1. Resistor vacuum furnace
2. Crucible.
3. Batch.
4. retort end.
5. Outer shell.
6. Thermocouple
7. Funnel.
8. Water cooling.
9. Gasket.
10. $MgCl_2$ can.
11. Water jacket.
12. Condenser shield.
13. Condensate.
14. Plates.
15. Support column.
16. Foot.
17. Clamp.
18. Vacuum outlet.

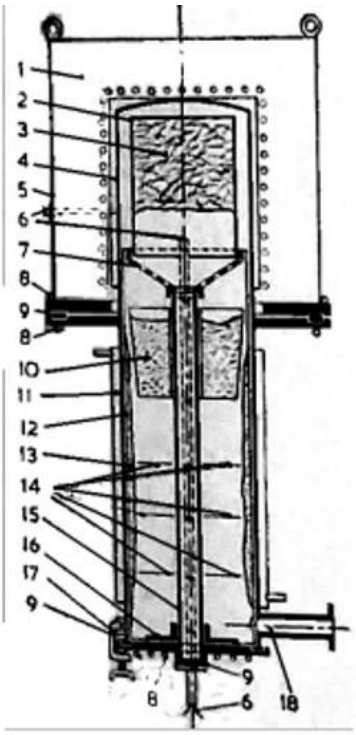


Fig. 8. Diagram of vacuum retort for the separation of magnesium chloride from titanium or zirconium sponge. (According to the U.S. Bureau of Mines, Albany, Oregon.)

Lower cost could result from heating a combined reactor retort with oil, thus avoiding also the heat losses occurring when down to room temperature between the two operations. However, since the heat must be applied externally, the wall of the equipment is exposed at high temperature to the full pressure of the atmosphere during the vacuum distillation period. This has,therefore, to be made of very heavy sections of heat-resisting steel, which represents a high capital investment. The external pressure also limits the size of the vessels because of the risk of collapse during the vacuum period. Any leaks in this case become a serious matter when they take place under the high external pressure of the atmosphere. This method, as far as could be ascertained, has been abandoned. Since the salt was tapped inside the reactor, and since the space had to be allowed for salt condensation and storage the apparatus was unduly tall and awkward.

A continuous process would permit cutting down the cost of titanium reduction, but the hopes that had been excited by some publications[50] have not been fulfilled up to now. As shown above, titanium sponge creeps on hot iron parts, to which it sticks intensively, which makes the use of pokers or mixers and of conveyors a doubtful proposition if not water-cooled. The temperatures involved in the magnesium reduction process are so high that even the best cobalt-bearing heat resisting alloys would barely perform satisfactorily from the point of view of mechanical strength and creep at the given temperature. If the temperature could be lowered below, say, 650°C., as, for instance, in sodium reduction according to a patent previously mentioned,[30] a continuous titanium reduction process might appear more feasible.

The possibility of substituting sodium for magnesium is worth examining. With sodium the reduction might be performed either below the melting point of its chloride, i.e., 800°C., between this temperature and the boiling point of the element, i.e., 880°C., or above this temperature in the gaseous state. All three propositions have been made. The second one leaves only 80°C. as operation margin. The last one runs into trouble with iron reaction with titanium which starts at 950°C. This may cause plugging of the sodium injector valve or sodium burner, which also are exposed to a build-up of metal and salts by local reaction. The first proposition is of great interest.

According to a recent patent,[30] the reaction between liquid sodium and $TiCl_4$ can be performed under noble gas at, for instance, 500ºC., at which temperature the NaCl produced is still solid, and, if a mixer is used, the mass obtained becomes granular and it can be moved. To stabilize the rather active titanium crystals obtained the reaction product is transferred to another vessel where the sodium chloride can mostly be separated by fusion and decantation under a noble gas, while the titanium crystals become deactivated to such an extent that, after cooling, the cake can be directly extracted with slightly acid aqueous solutions. It is not known whether a thermal vacuum treatment has to follow. Provided that the quality of the vacuum distilled, magnesium reduced sponge can be obtained also by sodium reduction, followed by leaching, especially as to the oxygen content, such a process would offer interesting price aspects, leaching being much cheaper than the vacuum procedure since it could be continuous.

The comparison of the two reducing agents, magnesium and sodium, must, however, be extended somewhat further. The power consumption in two electrolytic cells of similar capacity is about 14 kWh for the production of 1 kg. sodium, for 1 kg. Magnesium 20 kWh, and, when considering the different valencies and atomic weights, the power consumption is per equivalent about ⅓ higher for the production of sodium.[51] The same excess of heat is developed when reducing $TiCl_4$ with sodium instead of magnesium and sodium is a good reducing agent for magnesium chloride.

Heat dissipation problems in the sodium reduction are aggravated by the greater volatility of this element. The price of the reducing agent does when not matter much at the present time titanium sponge still sells at $4. 50/lb., and sodium is even cheaper in some countries than magnesium, on the weight basis. However, when it comes to considering ultimate price developments for titanium sponge, the higher power consumption for sodium will certainly play a role some day,as well as the fact that the recycling of the NaCl produced through a sodium cell is of little interest, the value of the compound being so low. On the contrary, magnesium produced from anhydrous $MgCl_2$ that is being reformed in the process through an electrolytic cell benefits from the fact that the price of this compound represents about a quarter of the cost of the magnesium electrolysis.

When using sodium only about 1 per cent reducing agent is needed as excess, but this is lost when leaching the sponge, while in the magnesium reduction, the excess has to be 15 to 20 per cent, which metal is, however, reclaimable, at least partly, in the vacuum distillation. Sodium is perhaps easier to clean and feed continuously, for instance through pipes, in a reactor, than is magnesium, and its low melting point is an advantage in handling. If the same quality of sponge can be obtained with both reducing agents, it is not impossible that sodium might have some price advantage, in so far as leaching can be cheaper than vacuum distillation, because it can be continuous. This might well compensate for the higher equivalent price to be paid for sodium on account of the higher power consumption in its production.

Magnesium Reduced Sponge

The impurities of this sponge, besides originating from the noble gas used in its production, from moisture and from leaks of the atmospheric air, are substantially those of the magnesium used, those of the titanium chloride and those introduced from the reactor crucible materials. The oxygen and nitrogen content can be kept below 0.1 per cent and 0.02 per cent respectively. By carefully vacuum drying the equipment used, the oxygen content could be lowered still more, as well as by gettering the noble gases employed. The magnesium, if made electrolytically, is rather impure and it introduces usually up to 0.1 percent manganese in the sponge. With silicothermic magnesium the manganese content can be held below 0.02 per cent.

In the vacuum distillation for separating the magnesium chloride, fresh crucibles and retorts release some manganese into the vacuum room at high temperature which may contaminate the first batch of sponge. The titanium chloride can be purified to the extreme as to silicon chloride, and oxychlorides contained can be eliminated by sufficient care in fractionating. The main impurity of the sponge is iron, mostly originating from the iron walls on which the sponge grows. It is of the

order of lees than 0.3 per cent for the grade A-1, less than 0.5 per cent far the more impure grade A-2 with reference to the product of one American company. He iron pick-up from the reactor walls depends on the time used in the reaction as well as on the temperature, which are both correlated. No special studies have been published as to the hardening by iron in high purity iodide zirconium, melted under carefully controlled conditions. Iron is not an objectionable impurity if this element is going to be added anyway a6 an alloying addition.

Depending to what use the sponge is going to be put, some other impurities such as silicon and carbon, might be tolerated, or would even be desirable to some extent, The magnesium content at vacuum distilled sponge may be up to 0.3 per cent and it may not be entirely unwanted because it stabilizes the arc in melting. Less than 0.1 per cent chlorine is desired in a good quality sponge, but frequently not found in commercial grades. Some oxygen is introduced in the sponge when conditioning it to the air after vacuum distillation and a slight temperature increase is noticeable at that moment, The sponge may even ignite spontaneously if air is admitted too rapidly. The hydrogen in an ingot made from vacuum distilled sponge originates mostly from the moisture absorbed on residual $MgCl_2$ or absorbed on the surface of the sponge, which is introduced by handling in the air, This moisture may also be tied up chemically with residual chloride. The sponge after vacuum distillation, should therefore be exposed as little as possible to air and it should be stored in tight metal cans. An argon blanket is not needed,

The extreme limits of purity of titanium sponge made by magnesium reduction have not yet been reached, Gettering of the reaction atmosphere and purification of the magnesium used by a pretreatment with $TICl_4$ hive not yet been resorted to, despite the fact that these means would permit lowering the impurity level still more. A sponge yielding fused buttons of a Brinell hardness of 170 is accepted, but a hardness below 150 is desired. In fact no specifications exist today as to the sale of sponge in the U.S.A. and tolerances are agreed upon between buyers and producers. American sodium reduced sponge with a hardness of 130 Brinell is being offered. Its iron content ts below 0:05 per cent, but it has a fairly large amount of chloride. Some selected Japanese sponge with a hardness of 100 Brinell is being offered.

No agreement exists as yet as to a suitable oxygen determination method for titanium. Combustion in dry HCl gas, which gives fair results for oxygen in zirconium, is unreliable. The vacuum fusion extraction, which is widely recommended, gives reproducible results only if equipment and method are strictly the same. The difficulties in oxygen determination are considerably increased with alloys or sponge since volatile constituents such as manganese and magnesium distil off, and condense in the cooler parts of the crucible where they usually react back with the carbon monoxide evolved. The lack of a rapid and reliable determination method for oxygen is interfering considerably with the development of this metal.

Melting and Casting

Since titanium reacts, when hot, with oxygen, nitrogen and moisture of the air, and since it picks up oxygen by reaction when melted on any oxide-base refractory,[8] normal melting procedures refractory oxide crucibles are out of the question. In 1946 it was shown that titanium and zirconium can be melted in graphite and with a graphite arc electrode.[10] While the carbon contamination in melting in graphite reaches not more than 0.3 per cent with zirconium, it can readily go up to 1 per cent and more with titanium, depending on temperature and contact time and the amount picked up is unpredictable. Nevertheless, melting in graphite, for instance, by high frequency induction, is established as a standard practice for the remelting of scrap and to produce castings because no better method is available. Graphite electrode arc melting has not yet fully been replaced by the consumable electrode process.

1. Windows.
2. Watch protection glass.
3. Conus.
4. Thoriated tungsten tip.
5. Brazed joint.
6. Water-cooled copper block.
7. Pyseal insulation.
8. Steel springs.
9. Water pipe.
10. Angle iron holder.
11. Insulation.
12. Soldered joints.
13. Brazed joint.
14. Bolt.
15. Flexible tubing.
16. Water-cooled copper block.
17. Base plate.
18. Trash tray.

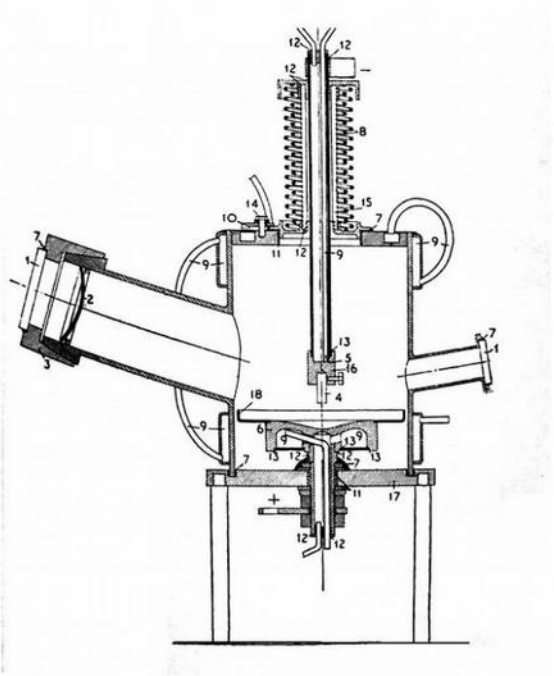


Fig. 9. All metal arc furnace for melting titanium and zirconium. Used in 1937 by Kroll.

A historical survey of the arc melting method may be welcome at this point. W. von Bolton,[9] the tantalum pioneer, used a direct current arc between a tantalum electrode and a water cooled copper plug to melt a tantalum scrap briquette, in a vacuum within a glass bottle. This furnace was seen in operation in 1932 and the author decided later to rebuild it fully in metal. The construction adopted[8] is given in Fig. 9. It was operated in vacuum broken with sufficient argon, to avoid a glow discharge. Thoriated tungsten electrodes were used at the time. In 1910 Weiss had already used consumable electrodes in the vacuum arc melting set-up shown in Fig. 10, to eliminate aluminium contained in zirconium aluminium alloys. The Kellogg Company introduced in the thirties a method for making iron alumina catalysts for oil cracking purposes, by arc melting a mixture a magnetite and alumina in a water-cooled copper sleeve, after which the material was ground and reduced with hydrogen. This process of fusion was so successful that the company decided to produce in this way special steels in small sections, thus greatly reducing the cost involved in rolling such hard materials.[53] At that time Junghans[54] continuous casting of metals in a water-cooled copper mould was already well known. In 1947 Parke[55] vacuum melted molybdenum rods, made by sintering in the melting furnace itself, in a water-cooled copper sleeve.

Thanks to the work of Gilbert and Beall[56] at the Bureau of mines station of Albany, Oregon, the arc melting of zirconium with the consumable electrode was actively and openly promoted and developed, while a similar movement went under way in secrecy with private companies.[57] This led finally to the construction of huge arc melting units of the type shown in Fig. 11. which are capable of melting up to 2 tons of metal in one operation.

Only a few of the most important aspects of arc melting can be considered here. These are: the type of current, the stirring of the bath, the electrode material, the conditions prevailing in the *vacuo* under the arc, and the construction of suitable melting chambers.

Since direct current is exclusively used, alternating current giving an unstable arc, high current DC generators must be provided for. These can be rotary sets, switched in parallel, but these require much maintenance and they fall off under load. Preference goes today today to selenium arc welding rectifiers in parallel which recover immediately under load. A number of electrodes can be operated simultaneously in the same furnace, provided each one has its own current generating unit and circuit.

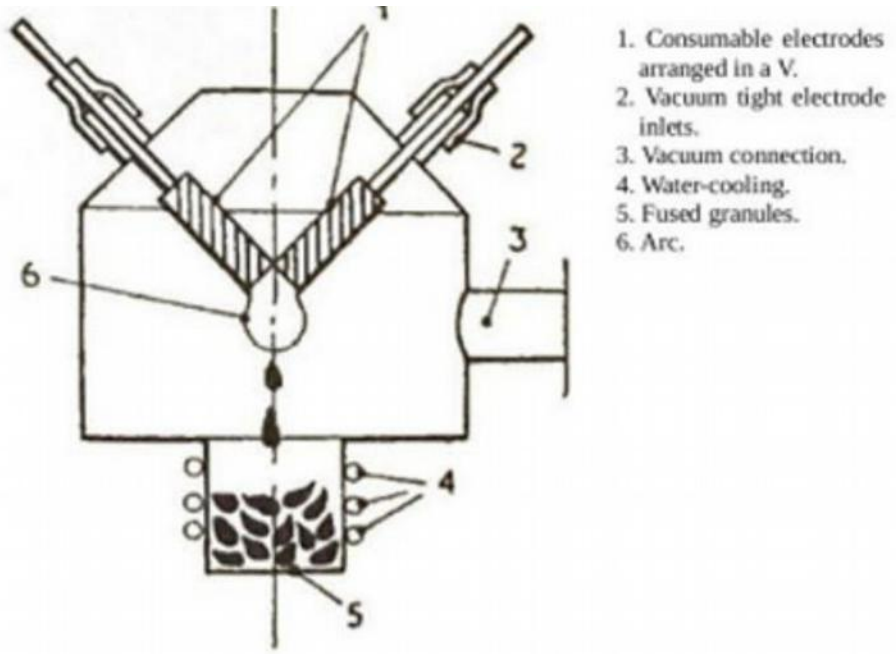


Fig. 10. Consumable electrode arc-melting in vacuo according toWeiss

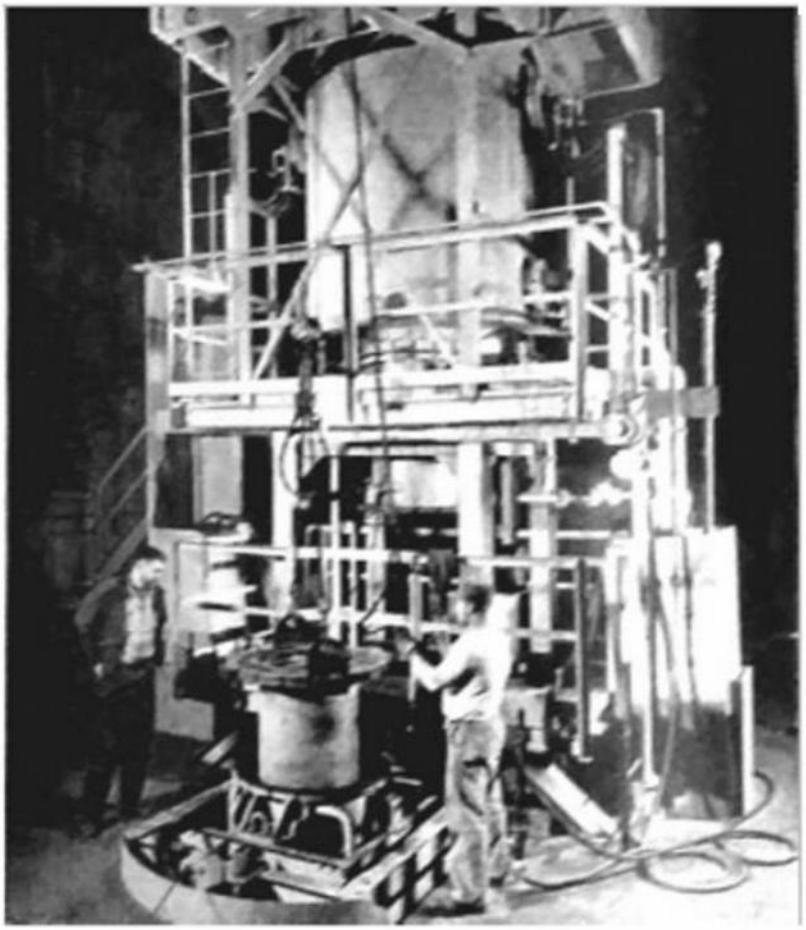


Fig. 11. Large one ton arc melting furnace as used at Henderson Nevada

Melting with a mechanically rotating, eccentric electrode is being given up in favour of the electromagnetic stirring of the bath. For this purpose a direct current coil, introduced by Gilbert and Beall, is arranged around the copper sleeve. It has a separate current supply and provides for adjustable mixing of the bath by way of a rheostat, which needs but little energy. This coil can either be movable along the vertical axis of the mould, to follow the rising arc and the bath level, or it may be arranged in a rigid position if long enough to cover the whole length of the ingot. The coil besides bringing about a rapid stirring, according to the principle of the homopolar electric motor, also centres and holds the arc so that it cannot strike the copper wall This evidently depends also on the shape and on the exact positioning of the coil. If the solenoid is flat and if it is located above a certain critical point of the arc, the magnetic flux, because of its curvature, may not pinpoint the arc, but may cause creation of a kind of umbrella, which, however, remains stable, while under the influence of the magnetic flow.

The coil having to perform two different functions, the stabilizing of the arc and the mixing of the bath, it is questionable whether this could not be achieved more conveniently with two independent solenoids. A third function of the coil is to lengthen the DC arc, which in a magnetic field travels along a spiral, thus giving it a voltage about one-third higher than without the coil, and consequently allowing a higher power input The whole atmosphere rotates around the arc, and impurities can be thrown out to the walls of the mould by centrifugal force.

The question as to what electrode material to use is not settled as yet, the self-consuming electrode is gaining preference. With graphite or tungsten electrodes there is always a risk that accretions may form on these, which after a while, may become hot enough to melt off and to cause local accumulations of W or C in the ingot. While these impurities could be accepted in small quantities, if evenly distributed, their local concentration might cause cracks and imperfections in the fabrication that follows. It is said that with graphite electrodes and with a magnetically well-controlled arc, the carbon pick-up may not exceed 0.05 per cent, which would be acceptable if the impurity was evenly distributed. A carbon content higher than 0.2 per cent reduces the impact strength and the weldability. Homogenizing the ingots with the object of dispersing the electrode impurities picked up by diffusion has never been reported. It may require comparatively high temperatures as well as the use of special and costly furnace equipment. Nothing is known as yet about the diffusion rates of impurities and of alloying constituents in titanium in function of the temperature and time. Homogenizing of ingots is common practice for a great many metals and it should apply quite as well and with advantage to titanium.

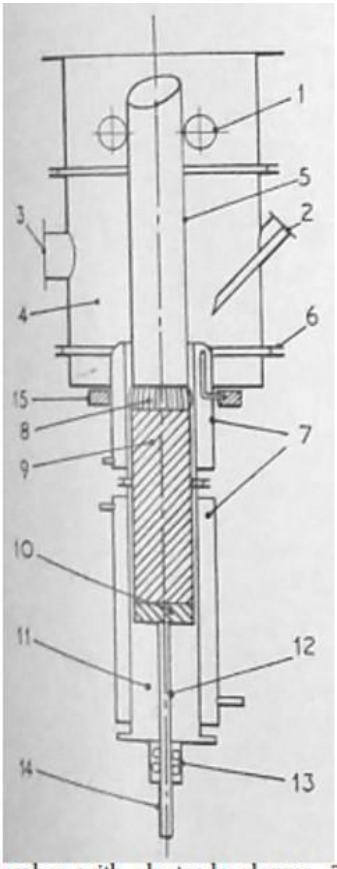
The consumable electrode could be made in the furnace itself by continuous stirring as done by Parke for molybdenum, but not been successful up to now with the rather coarse titanium sponge produced by magnesium reduction. Titanium powder, as produced in the fusion electrolysis, might be more adaptable to the Parke process.

Normally consumable electrodes are pressed from sponge outside the furnace, which operation requires heavy presses and is costly. Nevertheless, this latter method has been followed up and the pressed bars are welded together under noble gas in a tight box,[53] with a tungsten electrode forming staggered and interlocking packs which are assembled to a tall bar. Long electrodes cannot easily be handled in such a noble gas welding box and sections are prewelded as indicated and assembled in the furnace itself. This also cuts down on the height of the building and on the space needed above the furnace to handle the welded assemblies. These cannot carry the heavy current over the whole length since they are rather uneven and of variable conductivity and local overheating may take place whereby the welds may become unduly stressed. The electrical energy must, therefore, be applied close to the lower end by way of water-cooled rolls or slip jaws. Joining small briquettes of sponge by light pressure and by passing of heavy currents in an inert atmosphere with the object of welding them together in a pile might some day solve the problem of avoiding heavy presses.

Usually the first ingots produced are welded together and remelted as a self consuming electrode to yield a large size final ingot. This practice is common in the production of alloys because of the need for obtaining homogeneity and of eliminating surface inclusions. The second melting under argon or *in vacuo* can be simplified since the premelted electrode now conducts the

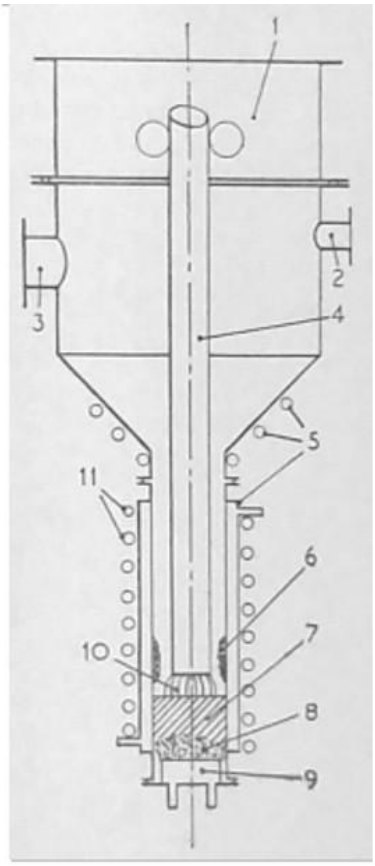
current well. The energy may now be introduced at the upper end and it can be allowed to pass through the well-conducting metal in its whole length. The current may be supplied through the water-cooled copper pipe, sliding through rubber O-rings and suspended as a simple mechanical gear. The joining of premelted ingots to produce the consumable electrode for the second melting may be performed either by nipping the machined ends of by arc welding them together under noble gas, with filler wire.

Frequently, especially if the power supply is too low, the impurities of the sponge, such as $MgCl_2$, are condensed on the wall of the copper mould, and if the latter is now being filled with molten metal, these might not be redistilled upwards but may become entrapped in the skin, causing imperfections. The question therefore arises whether one should maintain the bath at a constant level by continuous lowering of the ingot in function of its formation, or whether it is preferable to fill the mould, thus raising the bath level continuously. Both solutions are being employed. They are shown in Figs. 12 and 13.



1. Upper chamber with electrode clamps. 2. Feeder for alloy constituents. 3. Vacuum connection. 4. large vacuum chamber for condensate. 5.Consumable electrode. 6. Insulating joint. 7. Water-jackets. 8. Arc. 9. Retractable ingot. 10. Bottom plug. 11. Cooling chamber. 12. Lower electrode connection. 13. vacuum tight joint. 14. Connection with mechanical extraction movement. 15. Stirring solenoid.

Fig. 12. Arrangement of consumable electrode arc melting by the continuous casting method, batch level constant, ingot moved.



1. Upper chamber with electrode clamps. 2. Feeder for alloy constituents. 3. Vacuum connection. 4. Consumable electrode. 5. Water-cooling 6. Condensate. 7. Ingot. 8. Starting sponge. 11. Cooling chamber. 12. Lower electrode connection. 9. Water-cooled bottom plug. 10. Arc. 11. Cooling.

Fig. 13. Arrangement for consumable electrode arc melting with mould filling. Ingot remains in position, bath level rises.

It would seem that the continuous casting with constant level would be easier to achieve in the first melting operation the ingot produced is still not too heavy, so that a light extraction mechanism can be used, which is a desirable feature when operating in a vacuum. The advantages derived from a first melting *in vacuo* and from the continuous extraction of the ingot, are besides a stabler arc, that the condensates of $MgCl_2$ and Mg are not being entrapped in the melt at the cool

copper wall because they distil off above the constant bath level. This brings about a better ingot skin. However, it is said that continuous casting is feasible only with low chlorine sponge.

A large chamber can be provided for just above the bath surface in which the impurities can be collected without falling back in the melt as indicated in Fig. 12. Suitable space conditions for a rapid escape of gases can be created in this way at a short distance from the electrode tip. This permits a rapid vacuum degassing by reducing the length of the path which the gases must travel. The melting sleeve can be rather short and easy to replace compared with the long and more expensive mould represented in Fig. 13, which is filled up progressively with metal. However, the local wear is also heavier in a short sleeve with a constant bath level.

The question whether to melt *in vacuo* or under a noble gas is still not settled. It is intimately tied up with the presence or absence of hydrogen in the sponge. A hydrogen-bearing titanium should, by all means, be melted in a vacuum but if double melting is used, as is becoming common practice with alloys for purposes of homogenization, the second melting should be performed under noble gas, preferably in a mixture of 8 parts of argon and one part of helium, which gives a stabler arc.[59] For simplicity reasons the mould should be filled progressively with fused metal in the second melting since the extraction of a big and heavy would require heavy machinery. The first melting *in vacuo* eliminates volatile impurities such as $MgCl_2$ and Mg rapidly and a stable arc is obtained. Simultaneously most of the hydrogen is removed by dissociation of the hydride solution.

One may ask what quality of a vacuum should be used. Evidently, what is is measured as a vacuum at the gauges is not what appears under the arc or around the electrode since the gauges are applied on the cold furnace shell, and they measure only the cold, non-condensable gases. This measurement gives at best only a picture of the tightness of the furnace and it indicates the evolution of permanent gases of various origin, The bulk of the pressure under the arc is, however, a composite resulting from gaseous $MgCl_2$ magnesium, titanium, and hydrogen, besides that of some other minor impurities.

Nothing is known about the relative quantities of condensable and of permanent gases evolved from the melt, and of their partial pressures, but indications are that the total pressure at temperature under the arc is of an order of magnitude higher than that which the gauges register for the escaping cold, non-condensable gases. Besides this, one has to consider the free space available the escape of gases in the melting sleeve to obtain an idea about the pressure conditions under the arc and around the electrode shaft. The expression “pressure ” is used intentionally to indicate that a free flow of gases at high velocity that prevails in a good vacuum is not being dealt with, but a positive gas flow brought about by considerable pressure differences, where conditions of free path interfere little or not at all.

When using tungsten or graphite electrodes the surface above the bath is relatively little obstructed and the gases may more easily escape, but with a bulky consumable electrode the situation is very different. The section of such electrodes is made as large as possible to reduce their lengths and to make them more easy to handle. Therefore, the clearance between mould and electrode shaft is in this case narrowed down to the extreme limits of safety and usually a clearance of not more than a few inches allowed between the mould and electrode, This reduces greatly the possibilities of the gases escaping in the large vacuum chamber above the melt, the more so since these gases are driven off at high temperature at which their volume is increased about six times. A pressure build up under the electrode and in the narrow space between its shaft and the sleeve is thus unavoidable and is even absolutely necessary to avoid excessive titanium evaporation as well as glow discharge. The pressure-rise depends on the relative sections of the mould and electrode, i.e, on the space left between both, as visible in Figs, 12 and 13, as well as on the length of the path which the gases must travel before reaching the large condenser chamber.

The pressure of the element titanium at its melting point is of the order of about 5 microns.[60] It is evident that if a vacuum of the order of one micron could be maintained under the arc of a gas-free titanium, all the energy input would be used, disregarding radiation and conduction losses, for the evaporation of the titanium, which carries away all the heat for the phase change from liquid to gas. The metal would soon freeze because its temperature drop in function of the pressure

prevailing at the bath level, to the corresponding point of temperature related to the one micron | pressure of the temperature pressure curve, i.e., below the melting point of the metal. This is by no means different from evaporating water in a vacuum jar whereby ice is formed. Besides this, the phenomenon of gas discharge might interfere if a good vacuum was maintained around and under the arc.

When evacuating a room filled with argon, in which an arc is maintained between two tips of metal, there arrives a moment when the arc spreads in the room, because the ionized gases present are more conducting than the metal vapour of the arc. A glow discharge sets in, which is of the same nature as that of any neon sign. This phenomenon is ruled by the gas pressure and voltage, and it also depends on the nature of the gas. When continuing the evacuating, the glow discharge becomes weaker and it finally extinguishes completely. Naturally, the fusion of the metal stops long before, at the moment when the glow discharge starts. It can be seen therefrom, that a good vacuum cannot be maintained under the arc and that a compromise must be struck as to the pressure admissible for a rapid degassing while maintaining a steady arc.

The piling up of gases in the space under and around the electrode shows that the quality of the vacuum obtained by the the pumps is of minor importance considering the pressure produced by the obstructions put in the path of escape of the hot gases and the influence of dimensioning of the melting zone, provided the pumping capacity is high enough. Greater interest should be concentrated on the right dimensioning of the mould as to its length and diameter and to the cross section of the electrode. Melting *in vacuo* in a narrow and deep mould annihilates the effect of the best diffusion pump. How good should the vacuum be, as measured at the furnace shell? No figure can be given as to this since it also depends, disregarding the just-mentioned geometry factors of the mould and electrode, on the content of the sponge in volatile impurities. The pumps should have a volumetric capacity high enough to permit lowering the hydrogen in the ingot to less than 60 p.p.m., and the absolute vacuum at the pumps microns is of minor interest. The quality of the vacuum can and should be better in a second melting of the already degassed metal, provided it does not drop so low that on one hand excessive titanium evaporation would occur, and that on the other hand there would be no possibility of a glow discharge.

Degassing titanium may not only be a simple volatilization of impurities such as magnesium and its chlorides or the liberation of a dissolved gas such as hydrogen. Titanium nitride is known to dissociate slightly at high temperatures and repeated arc melting may therefore have a softening effect because of denitrification. It has never been observed that any reaction took place in the best vacuum in a carbon-bearing titanium with a few tenths of a per cent of dissolved oxygen. As to hydrogen elimination, bubbles observed in titanium ingots that froze under argon of atmospheric pressure indicate that titanium retains this impurity in the fused state which is partly liberated on freezing, possibly because of a differential solubility in the liquid and solid state.

One of the basic principles of vacuum metallurgy is that the gas evolution or the evaporation of constituents of a fused, well-mixed bath takes place only at the surface, where the hydrostatic pressure does not interfere. Consequently one has to increase the bath surface for a rapid vacuum degassing. The arc vacuum furnace in its present form with a long and deep melting sleeve is not well adapted for this task because of its narrow evaporation surface. Some gas evolution can also be expected from the electrode and from the drops of fused metal that fall in the bath, but the time given for evaporation is short.

If high vacuum degassing with consumable electrodes was considered, the arc melting arrangement in a V, as shown by Weiss[52] (see Fig. 10), would be preferable to the high frequency melting suggested by Magel,[61] because of the large space of escape for the gases provided for around the electrodes.

The Production of alloys by arc melting encounters various difficulties which refer to the even distribution of additions over the the ingot and to losses by volatilization. Little is known at present about alloying techniques used industrially, but complaints about inhomogeneity are so frequent that one can surmise that solutions have not yet been found. Gilbert[56] adds the ingredients in the form of round pills, with a mechanical distributor in function of the rate of fusion. The additions of

the brittle constituents such as manganese may be enclosed in an aluminium wrapping if both metals have to be introduced. Titanium being lighter than most common metals, the heavier additions may drop through the bath and freeze to, and remain unalloyed on the bottom. This phenomenon has been observed even with additions of the readily fusible tin.

If volatile metals such as manganese become stuck to the copper mould at the bath surface, the arc may strike them and volatilization loss occur. The use of readily fusible, now available master alloys such as those of titanium with A, V, Fe is recommendable. Evidently any high manganese alloy will lose some of its alloying element if melted or remelted *in vacuo*, if care is not taken that a residual gas pressure prevails in the arc area, high enough to meet the temperature pressure conditions needed for holding the manganese in the metal. A high vacuum, in this case, may be pernicious. Oxide and nitride when present in the sponge as specks, are not at all readily absorbed by the melt and if the melting is fast, which leads to a cool bath, the inclusions may remain undissolved, which causes local brittleness when processing the ingot to sheet.

The ingots of the first melting cannot, of course, be removed immediately after freezing because of the risk of surface oxidation and carry-over of oxide to the second fusion. One has to wait until they have cooled down to a temperature at which the air does not react. Considerable capital expenditure results from the fact that the furnaces for the first melting operation thus cannot be used during the the cooling period of the ingots. Devices may be found to remove the ingot immediately after freezing, for instance by using a noble gas blanket in the mould wile it is displaced, but nothing had been published about such a complicated arrangement.

After melting and withdrawing the ingot, the furnace may be used again, provided it has not been exposed unduly to the humidity of the atmosphere. Its internal surface is covered with hygroscopic material, especially magnesium chloride and pyrophoric magnesium, which easily absorbs humidity. The latter may be released in the next run, causing hardening of the metal, as well as adding hydrogen to it. Therefore, the furnace should be held sealed, eventually under vacuum, and a frequent cleaning is necessary. The pyrophoric condensate constitutes an explosion and fire hazard. In view of the need for cleaning, all inner mechanisms must be of simple construction and as smooth as possible. The electrode clamps and connections as well as the feeding device should be arranged in a chamber where they are less exposed to the condensable impurities given off during melting. The titanium ingots, after melting, may have surface imperfections of various kinds, as blow-holes and entrapped chlorides. The surface can be smoothed by a process developed by Gilbert and Beall at the Bureau of Mines station in Albany, Oregon, called suitably, “arc machining”. The ingot, held between point in a simple lathe, and running under noble gas at low speed, can be superficially fused with an arc, struck between a tungsten tip and the metal. Machining to eliminate the surface defects usually results in a loss of 10 – 15 per cent of metal, while “arc machining” does not bring about appreciable losses except small unavoidable ones on both ends, which have to be turned off on a lathe. “Arc machining" closes voids and pinholes, while turning on the lathe frequently opens them. Surface arcing had already been recommended before for the smooth surfacing of quartz tubes with an arc struck between carbon electrodes.

Casting titanium raises the problem of crucible and mould materials. Scrap recovery is intimately tied up with the same questions. Graphite is the only less reactive crucible and mould material used up to now, but as to the latter, some carbonaceous or some oxide materials which are difficult to reduce, such as stabilized zirconia, may, perhaps, be considered too, Dead burned or fused calcium oxide could be recommended but only when used at atmospheric pressure, with a metal that is not overheated, since titanium reacts *in vacuo* and at high temperature with this oxide. To avoid a contact of fused titanium with carbon one can melt with a temperature gradient from the bath through the graphite to a refractory so as to maintain a skull[62] of solid titanium in contact with the graphite, the diffusion of carbon through the solid titanium being very slow, This temperature gradient can be obtained by a skilful use of refractories, permitting a control of heat dissipation, Besides this method, low pressure arc melting with a high energy input in a water-cooled copper sleeve, as can be performed under certain conditions of arc operation, may yield a large pool of fused metal which is available for tapping or for pouring over the rim.

A similar method with bottom tapping was developed by Simmons,[59] who arc melts in a cooled graphite box with a central tap hole. Titanium being extremely fluid even without over-heating, fills even an intricate mould perfectly. This process is therefore also recommendable for foundry work.[59,62] Finally, titanium can be fused out of contact with any crucible material by “levitation melting” with high frequency currents.[57,63] This process, which is quite successful on a laboratory scale, is under development, but difficulties occur with larger batches from the fact that there is no oxide skin to contain the fused titanium in a kind of egg shell, as is the case with aluminium, since titanium has the property of dissolving its own oxide,

Scrap Recovery

At Present the quantities of titanium scrap offered in the American market are estimated at anywhere between 250 and 1000 tons, which are available at from 0.40 to 1.25 dollars/lb., depending on purity.[64] The purchasing price of processed sponge being between 9 and 15 dollars/lb., it is understandable that the users of titanium are looking for a market for their scrap, which frequently represents 50 percent of the weight that went into fabrication. One has to define what is meant by scrap, and it is evident that the various kinds available are not equivalent as to quality. Clean, pure titanium scrap can be remelted in a carbon or tungsten arc furnace with normal sponge, to which it can be added in amounts of up to 30 per cent, provided the final oxygen content introduced by the scrap and sponge does not exceed the tolerable level. When melting sponge with a consumable electrode only little scrap, carefully sized, an be added because of the difficulties of introduction. Castings can be made by scrap melting in graphite crucibles heated by high frequency currents, but their usefulness might be limited because of the presence of carbon, which impairs corrosion and mechanical properties. It is not known to what extent skull melting is being used for the production of low carbon castings.

Alloyed scrap has to be kept separate and it must be added in the arc melting of alloys of the same kind. Mixed alloy scrap is mostly worthless. Great difficulties arise when oxidised metal has to be reclaimed. The oxide may not even be apparent at the surface, since the visible one may have been pickled off, but enough may remain invisible in the diffusion layer of the skin, beside nitrogen and hydrogen. Worse still is the heavy scrap that may result from bad forging and pressing operations. This may be cracked deeply with oxide coats in spots inaccessible for mechanical cleaning. Also breaking up and sizing such heavy scrap is no easy task considering the high mechanical strength of the metal and its property of building up on cutting tools.

Other methods of scrap recovery besides remelting are hydrogenisation to embrittle it followed by grinding under organic fluids and use of the powder produced in powder metallurgy; production of ferro-alloys free of aluminium, silicon and carbon to be used especially in stainless steel production, assembling packs of clean sheet metal b welding the rim to metal to thinner sections for re-use; casting of the scrap in electrode form for purification by fusion electrolysis; and production of $TiCl_2$ from scrap and $TiCl_4$ and disproportionating the former.

Hydrogenisation can be performed successfully only with thin sections and powder metallurgy does not offer a big outlet on account of the high cost caused by vacuum sintering. The steel industry could absorb a good tonnage of scrap titanium, transformed into ferro-alloy, but the obtainable price of about $2.60/lb., of titanium is low. Reassembling sheet sections by welding applies only to very specific cases of clean, oxide free, sheet scrap. Usually this can be more easily processed by arc melting. The fusion electrolysis would be quite attractive if the many problems of running a big cell with soluble anodes, as described above, were solved, The $TiCl_2$ disproportioning has not yet left the laboratory benches.

General Properties

Very few metals combine such vicious and such wonderful properties as does titanium, Since oxygen and nitrogen, once they contaminate the metal, cannot be eliminated or neutralized by any means or reagents, a vacuum or a noble gas atmosphere must be used whenever it is exposed to a temperature high enough for a rapid pick-up and diffusion of these impurities into he matrix,

Hydrogen has only recently been fully recognized as a very dangerous impurity in titanium, It may be introduced through contaminated sponge, when melting the latter under a stagnant noble gas at atmospheric pressure instead of using a vacuum. This impurity may also be due to pickling in a fused NaOH/NaH bath or in a solution of HNO,/HF[65] containing too little nitric or too much hydrofluoric acid,[74] The Virgo fused NaOH/$NaNO_3$ salt used at low temperature, is said to introduce only tolerable amounts of hydrogen,[66] Humidity and furnace gases can react at elevated temperature with titanium, which they contaminate with oxygen and hydrogen, The obnoxious effect of hydrogen on titanium and on its alloys is quite complex, and it may be enhanced or reduced by other impurities and by alloying additions. Lenning[66] and McQuillan[67] show that the solubility of hydrogen in alpha titanium is about 170 p.p.m. at about 300°C, and it is practically nil at room temperature, Precipitation of hydride takes place within this temperature interval, especially on strain.

TABLE I – NOTCH IMPACT STRENGTH

Temperature °C	Notch Impact Energy ft-lb	
-	H_2 – 10 p.p.m.	H_2 – 100 p.p.m.
100	14	6
25	2	4
-40	5	5

TABLE II – CHANGE OF PROPERTIES WTH TEMPERATURE

Temperature °C	U.t.s lb/in^2	Elongation in ½"
100	54,000	46
25	73,000	16
-40	85,000	31
-160	136,000	18

The mechanical properties of hydrogen-bearing titanium and titanium alloys change on storing. Hydrogen has a bad effect on the notch impact and notch bending strength and it enhances the strain rate effect. Its action in alloys containing beta titanium is less pronounced, and titanium molybdenum alloys are rather little affected by its presence.[66] While hydrogen has little action on the strength of titanium, it reduces the notch impact strength abruptly at the 200 p.p.m. concentration and shifts the brittle/toughness transition temperature point. The hydrogen influence on an 8 per cent titanium manganese alloy[66] as to notch impact as a function of temperature is given in Table I. Unnotched specimens showed barely any change with temperature.

It is generally accepted today, that titanium alloys should not contain more than 60 p.p.m. hydrogen after fabrication. The more beta titanium the alloys contain, the less sensitive they are for hydrogen. The hydrogen present can be pumped off by annealing i*n vacuo*. Hydrogen equilibrium pressures have been reported.[66] The solubility of hydrogen at 1 micron is about 24 p.p.m. at 715°C, and 15 p.p.m. at 865°C. The degassing *in vacuo* is quite rapid. A ¼ in, rod with 43 p.p.m. hydrogen lost about 60 per cent of this impurity in a 40 min. treatment at 815°C. Naturally, such vacuum treatment, if it had to be applied to finished parts, would have to take place at temperatures and for a length of time which would not bring about recrystallization.

Early experiments with titanium alloys showed considerable stray values as to notch sensitivity and fatigue strength and this subject is still somewhat controversial today.[68] It seems, however, that titanium alloys are more notch sensitive than corresponding stee1s. It is not known how far the gases that penetrate the skin produce notch sensitivity.

The inversion temperature from the brittle to the tough state as observed with commercial titanium and with its alloys, is nothing unusual for metals in general. It is shared by the element iron, and the cracking of welded ships navigating in great cold illustrates this case, if we disregard the complications due also to welding. Structure materials used in planes are normally exposed to great cold, and stainless steel of the austenitic type as well as Duralumin are free from this low temperature embrittlement. It can be understood that titanium alloys used in planes should not show

any considerable alteration of their mechanical properties within the temperature range in which they must operate. Table II shows how commercial titanium changes its mechanical properties in relation to temperature, according to Lenning.[66] It can be seen that the elongation drops from 100°C. to 169°C. By more than 50 percent, while the tensile strength is more than doubled. Few data are available as yet as to the low temperature behaviour of titanium alloys, Spretnak[69] examined the alloys RC-30B with 0.24 per cent C, 3.8 per cent Al and 3.8 percent Mn, and the alloy Ti-150A with 1.3 per cent Fe, 2.7 per cent Cr, trace of C, at room temperature and at — 78°C. The already low impact strength of these alloys was reduced for the first one to almost 50 per cent, that of the: latter to 40 per cent of its room temperature value. Iodide titanium ts not susceptible to embrittle ment by cold. Some eutectoid, rapidly cooled beta-bearing alloys show severe embrittlement when exposed for a long tine, especially under stress, to temperatures between 400 and 800°F., i.e, in a temperature area below and above that of the eutectoids,[63,70,71] Alloys with manganese in combination with aluminium and aluminium bearing alloys in general, which are more of the alpha type, are said to be exempt from annealing embrittlement,[70] In the systems of titanium with iron[72] and with chromium, the transformations around and below the eutectoid temperature are sluggish, and long time annealing, as may happen in applications for which such alloys have been recommended in the past, may result in segregation of the “omega phase “ or in concentration changes, called “clustering" by McQuillan,[72] with pernicious effects on the malleability of the alloys. Ageing, as observed with certain alloys, may add to these troubles, which are the subject of recent publications.[73]

The enormous wear resistance and chemical activity of the metal causes a large consumption of grinding wheels, which may react chemically with titanium, when high speeds and pressures are applied, The galling of titanium makes machining and forming difficult because it builds up on the edge of cutting tools and it sticks in pressure forming or drawing on the dies, Plating, oxidizing and phosphate coating have been resorted to as a remedy against sticking, Galling interferes with the use of this metal in parts subject to frictional movement, This property impedes its use for gears. Nitriding and carbide coating are recommended in this case but, unfortunately, these must be applied at temperatures too high and grain growths and embrittlement take place All alloys , except those with aluminium and tin, give brittle welds on fusion welding, Alloys are usually strong and they harden when deformed in the cold state, which makes forming a difficult operation and fabrication in heated dies becomes a necessity. The need for a soft age hardenable alloy to facilitate forming is evident. The scrap problem is still waiting for a solution. Remelting in an arc furnace is possible, but the oxygen of the scrap hardens the ingot made, Unfortunately, alloys develop orientated properties on rolling, and turning in right angles becomes a necessity. This limits the size of the sheets obtained to that of the width of the rolls and strip milling cannot be applied to most alloys.

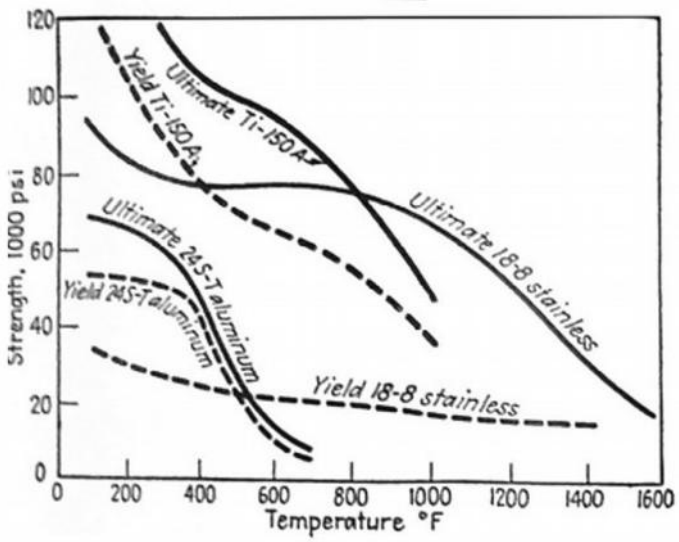


Fig. 14. The ultimate and yield strengths of alloy Ti-50A compared with steel at medium temperatures.

The low Young's modulus, less than 60 per cent that of iron, causes high deflections of titanium under load. The strain rate in in tensile strength determinations has a profound influence on the elongation data obtained and a fast rate may double it. A similar behaviour has been observed for molybdenum and tungsten. Creeping at room temperature is considerable but preliminary cold stressing alleviates it.

To this crushing enumeration of vices one may oppose a list of excellent titanium properties. First, there is its high strength to weight ratio. Its corrosion resistance to chlorides, especially to seawater, is outstanding and it can be used also in the most aggressive solutions of $FeCl_3$ and $CuCl_2$, as well as in wet chlorine. Maritime applications are most attractive, as, for instance, the hull of Navy planes, in the discs and blades of the compressor parts of gas turbines used in such planes, where stainless steel might corrode. Low specific gravity combined with high strength especially at temperatures between 200 and 400°C., where titanium is superior to stainless steels (see Fig. 14), may bring about weight savings of up to 50 per cent in gas turbine wheels and blading. Titanium firewalls in aircraft can be used up to 1100°C and they resist thermal shock well, The resistance of titanium alloys to water cavitation and to steam erosion is said to be much better than that of stainless steel. The shell impact resistance of the alloys is remarkable and it is said that weight savings of 15-25 per cent can be accomplished with titanium alloy armour plates.

Titanium is not subject to stress corrosion except under the most severe conditions. The chemical attack is usually smooth and free from pitting. Titanium is inert to body fluids and its high strength suggests its use in surgery.

It is not intended to expose here the physical metallurgy of the alloys which has been worked out quite well and which can be looked over in the specific literature.[74,75] However, some practical aspects of the use of titanium will be sketched below. The hardening effect of the metal by interstitial elements such as nitrogen, oxygen, carbon and hydrogen follows this enumeration in falling order, the latter having but little action. Fig, 15 shows the very rapid hardening of titanium by small additions of the three first elements as well as the corresponding lowering of the elongation. Carbon hardens relatively little but it reduces weldability, resistance to shock and to

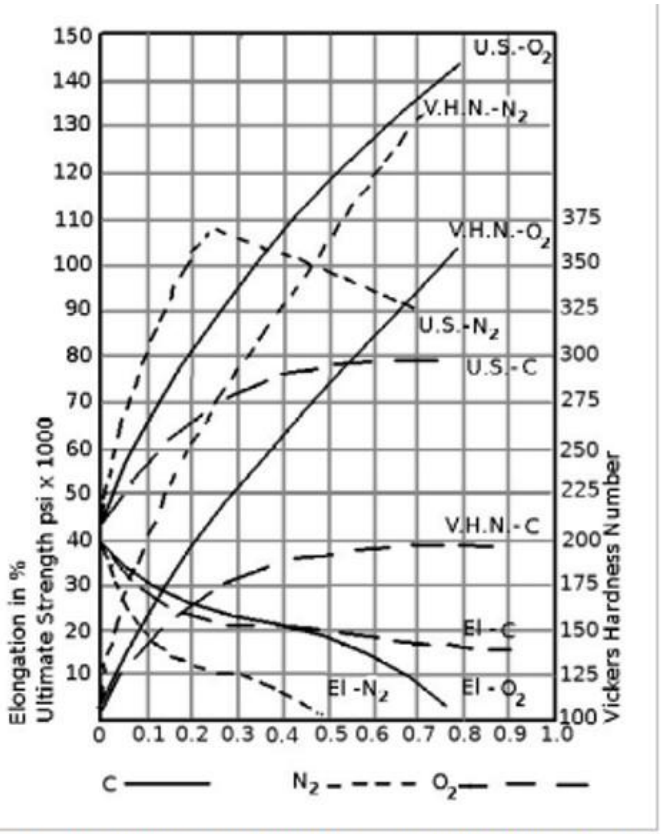


Fig. 15. Elongation, Ultimate strength and Vickers hardness of titanium as a function of oxygen, nitrogen and carbon.

corrosion, The elongation of iodide titanium is lowered with 0.2 per cent nitrogen, oxygen or carbon from 40 to 12, 27 and 23 per cent respectively.

At present a titanium sponge giving a hardness of less than 150 Brinell after melting, with an oxygen content of less than 0.07 per cent, nitrogen less than 0.02 per cent and hydrogen below 60 p.p.m., and a trace of carbon is considered as being of good quality. The hardness test is usually made by button melting with a tungsten electrode under argon and due to the chilling effect of the mould, variations of at least ± 5 points can be expected. Impurities such as Fe and N_2 may enhance the chill effect and may contribute to the hardness variations. Iron is frequently a constituent of titanium alloys. However, if iron free alloys are desired, most of the sponge on the market does not give satisfaction. American A-1 grade, for instance, contains up to 0.3per cent Fe. Japanese sponge with less than 0.1 per cent Fe is usual and metal from the same origin with a hardness below 130 Brinell can be bought. Iron may contribute to the medium temperature embrittlement of certain titanium alloys. The claims as to its inoffensiveness[63,74] should be re-examined, especially for complex alloys exposed for a long time to medium temperatures.

The main mechanical properties of various commercial alloys are given in Table III.

Aluminium and tin are now considered as the most promising additions for titanium. Both raise the transformation temperature, narrow down the mixed alpha beta field and produce alpha alloys that have high strength at medium temperatures, while being weldable by fusion, The properties of a 5 per cent Al, 2.5 percent Sn alloy at 600°F are given as follows: U.T.S. 65,000lb/in^2, yield strength 46,000 lb in^2 : and elongation in 2 in. 17 percent. While many alloys have been reported with a U.T.S. of 120,000 lb/in^2 at 800°F all these have shown embrittlement in 1,000 hr runs at this temperature.

Manganese titanium alloys are recommended for their good bending properties for sheet work.

TABLE III

PROPERTIES OF COMMERCIAL TITANIUM ALLOYS

Designation	Composition per cent	Kind	U.T.S. lb/in^2	Yield Strength lb/in^2	Elong^2 % in 2”
Ti-150A	2.7 Cr, 1.5 Fe	Forged	135,000	120,000	12
Ti-155AX	0.9-1.7 Fe, 0.8-2.0 Cr, 0.8-2.0 Mn, 4.74-6.0 Al	Forged	155,000	140,000	12
RS-110	4 Cr, 2 Fe.	Forged	120,000	110,000	12
RS-120	8 Mn.	Sheet	130,000	120,000	12
RC-130B	4 Mn, 4 Al.	Forged	140,000	130,000	10
A-110AT	5 Al, 2.5 Sn.	Sheet	120,000	110,000	10

Fabrication

A brief outline of fabrication problems and processes[74] will now be given. The titanium ingots, as they come from the arc melting, are machined superficially to remove surface imperfections. They are heated up usually in furnaces fired with oil or natural gas, but the flame should not impinge on the batch. This practice is being revised from the angle of hydrogen pick-up and electric heating is taking over. Forging is done either in presses or with hammers, the former being preferable[78] on account of the possibility of slow and deep deformation which reduces the risk of cracking. The forged ingots are then rolled in ordinary steel blooming mills, but the revolutions must be reduced to ½ compared with those used in stainless steel rolling, the metal being sensitive to a rapid deformation. The plates obtained are, after cooling, cleaned by heavy grinding with wheels mounted on a beam. They can, after reheating to medium temperatures, be rolled like stainless steel.

The removal of defects in titanium alloy sheets is not easy since the whole sheet must be heated up to intermediate temperatures because it would crack when cold ground at the spot where the grinding wheel is applied, on account of the thermal expansion and low ductility. Cleaning of sheets

for removal of a thin oxide coat has been done up to now either in a sodium hydride bath, in a So-called Virgo or sodium nitrate/hydroxide bath, or mechanically by steel shot blasting, the latter method now having preference on account of the fact that it does not offer much possibility of introducing hydrogen. The finish pickling can be done with HNO_3/HF solutions, provided the former acid is held at a concentration higher than 20 per cent and the latter below 2 per cent.[65]

The oxide visible at the surface is probably the less harmful one. It has been shown that diffused surface oxygen that is invisible increases the tensile strength and reduces the elongation of the metal, and that pickling such material brings the original good bending properties back, despite the fact that some hydrogen may soak in. Recently, finished titanium parts were submitted to a vacuum treatment below the recrystallization temperature it is claimed that the better properties obtained are to be attributed to a dehydrogenization. This might be true, but oxygen diffusion into the metal is more probably a factor n the improvement. The surface defects and hardness caused by oxygen might well be responsible for a part of the trouble with low impact and fatigue strength. All straightening of alloyed material must take place in the hot state. Wire drawing is performed on oxide coated material, deep drawing on phosphate coated sheet.[79] Extrusion is now being studied.[80] Good results have been obtained in presses capable of extruding steel. High velocity is essential to avoid excessive die temperatures, dies usually being made of sintered hard metals. Tubes have been produced by extrusion but these can also be obtained by welding a round strip of titanium under noble gas and drawing to the desired diameter. Extremely thin sheet is being made on Sendzimir mills.

Uses

At present about 80 per cent of all titanium made in the U.S.A. is used in the unalloyed form and practically all of it goes into military applications. These concern the navy, army and aviation. The former is interested in the use of titanium, for instance, in Snorkels for submarines, where corrosion from exhaust gases combines with seawater action. The second wants titanium for its lightness combined with strength for all equipment which must be transportable or airborne. The case of a mortar base plate has been referred to in the literature. Alloyed titanium for armour plates is a large field of possible use with considerable weight savings. The protection of the aviator with such alloy plates is indicated. The main present and prospective use is in aviation and in guided missiles especially when aerodynamic skin heating must be coped with. The question as to where to use titanium and its alloys in a plane has been examined by Teed[82] and Hanink.[68] The latter found that a commercial titanium alloy that could be considered as a substitute for a high quality steel in connecting rods of aeroplane engines had as good a strength in the polished unnotched state as the steel, but only one fifth of it when notched. These properties dropped also in the notched steel sample, but not as much as that and part of the drop could be restored by shot blasting, which latter is harmful to titanium. However, it is still not definitely established how notch sensitive titanium really is.

A serious competitor for titanium alloys, also at medium temperatures, appears to be the age hardenable stainless steels, which the author recommended in 1931,[83] and which are now under serious consideration. The elements Ti, Al, Mo, Mn, Si in combination with nickel confer age hardenability to steel in general.[84] A stainless steel of this type mentioned by Bedford gives a tensile strength of 195,000 lb/in^2, a yield strength of 182,000 lb/in^2, besides 19.5 per cent elongation. Another steel indicated by Lena[86] shows at 800°F a U.T.S. of 179,000 lb/in^2 and an elongation of 13.5 per cent. Such steels display a high yield strength, which does not drop much at medium temperatures. The advantage of hardenability by ageing, which permits processing in a soft state will be appreciated.

In aircraft construction, the life of a part made of titanium and its initial cost decide the possible advantage of substitution with regard to payload saving. The motor would take titanium wherever medium temperatures and high strength are concerned but some of the obnoxious properties mentioned above have yet to be overcome before applications will become possible.

Unalloyed titanium is used in engine nacelles and in landing gear doors of a commercial plane with 200lb weight saving and in tail assemblies of jet fighter planes to replace stainless steel. It is evident that in high performance planes the price of the metal plays a smaller role than in commercial aviation. Experiments are being made with titanium alloy wing coverings and frames. The fastener problem is under examination, too.[87] Since high strength alloys must be used for rivets so as to save weight, the riveting must be done in the hot state because alloys are not ductile enough and work hardening is too rapid. Extra strain as caused by the contraction of the metal is, however, introduced in hot riveting. With bolts, galling in the threads is a nuisance; that is being overcome by various means, for instance by plastic coatings. Besides this, notch sensitivity and relaxation in the threads under high load interfere in this application.

The Future

An inquiry made by Senator Malone[88] in the U.S.A. has thrown some light on the conditions of the slowly-growing American titanium industry. The present demand of aviation alone may be estimated at 100,000 ton/yr., but the sponge produced up to now at the rate of not more than 3,000 ton/yr. has been partly put in the stockpile. This seems rather odd, The main reason is that usually a dimensional change must be made in an aircraft part whenever one switches from stainless steel to titanium and there is no possibility of rapidly changing over again in the case of non-availability of titanium. Such design modifications cannot be accepted if the supply of titanium sponge is not guaranteed under all circumstances. Considering the small annual production of the metal, one single aircraft part might draw a very large proportion of the supply. The development of a larger titanium industry is also greatly handicapped by the scarcity of trained titanium metallurgists, which fact is not astounding, considering the special knowledge required for making and processing this unorthodox metal.

The daily production of sponge may now reach 20 tons with only three companies operating. Estimates foresee a production capacity of upwards of 20,000 ton/yr. by the end of 1957. All producers are under the threat of a new and much cheaper process being discovered, The risk of this is mostly taken over by the U.S. Government. As shown in this report, there is at present barely any new process visible for use in the near future, which might radically change the price of the metal. The fusion electrolysis has to overcome enormous technical difficulties before becoming practical, and its introduction is still far off. The substitution of sodium for magnesium is probably not going to reduce the sponge cost appreciably. Much more can be expected from progressively lowering the price of titanium chloride which, today, represents about 60 per cent of the sponge cost. A lot will also be saved if the cost of melting and fabricating of the metal can be reduced. One pound of titanium in the ore is worth less than 2 cents, as sponge $4.50, as ingot about $6.00 and as sheet around $15.00, The manufactured part is usually many times more expensive. This enumeration shows where the most promising savings could be made. Organized scrap[78] reclaiming would considerably reduce the very high fabrication cost.

Titanium must be considered as a prospective substitute for stainless steel, where it permits saving large amounts of scarce alloying elements such as chromium and, especially, nickel. With he depletion of high grade nickel ores, which has already forced the metallurgist to resort to ores with less than 1:5 per cent Ni, titanium seems to have a very bright future.

REFERENCES

1. J. J. Berzelius, *Pogg Ann.*, 1825, **4**, 1.
2. L. F. Nilson and O. Petterson, *Z. Physical Chem.*, 1887, **1**, 27.
3. M. A. Hunter, J. *Amer. Chem. Soc.*, 1910, **32**, 330.
4. A. E, Van Arkel and J. H. De Boer, *Z, anorg. Chem.*, 1925, **148**, 345.
5. L. Weiss, Germ, Pat. 314,791, 1919.
6. K. Seubert and A. Schmidt, *Ann. Chem.*, 1892, **267**, 235.
7. H. Freudenberg, U.S. Pat. 2,148,345, 1938.

J. S. Smarko, *Fiat Report* 798, 1946, PB 31,246.
8. W. J. Kroll, U.S. Pat. 2,205,854, 1940 and *Trans. Electrochem. Soc*., 1940, **78**, 35.
9. W. Espe and M. Knoll, "Baumaterialien der Hochvakuum Technik," Springer, 1936, Von Bolton, 36.
10. W. J. Kroll, C. T. Anderson, H. P. Holmes, L. A. Yerkes and H. L. Gilbert, *Trans. Electrochem. Soc*., 1948, **94**,1.
11. G. Volkert, *Archiv. Eisenhutlenwesen*, 1948, **19**, 1.
12. C. J. Stoddard, S.S. Cole, L. T. Eck and C. W. Davis, Bureau of Mines; R.I 4750, 1950.
13. A. W. Knoerr, *Eng. Min. Journ*., 1952, **153**,(3), 72, 76.
14. H. Sigurdson and S. S. Cole, *Trans. A.I.M.E.*, 1949, **185**, 905.
15. D. L. Armand and S.S. Cole, *Trans. A.I.M.E*., 1949, **185**, 909.
16. Ch. H. Moore and H, Sigurdson, *Trans. A.I.M.E*., 1949, **185**, 914.
17. F. H. McBerty, *Fiat Final Report* 774. PB 22,626, 1946.
18. P. J. Maddox, *Journ. Metals*, 1954, **6**, 734.
R.L. Powell, *Chem. Eng. Progress*, 1954, **50**, 578.
19. H. H. Hall and J. T. Kemp, PB 44,675, 1945, Item 21.
R. M. Hunter, *Cios Report* PB 204, 1948. Item 22, File XXIV.
20. G. Pascaud, *Compt. Rend*, 1950, **231**, 1232.
21. G. Rauter, *Ann. Chem*., 1892, **270**, 235.
22. A. Pechukas, assigned to Pittsburgh Plate Glass Co., U.S. Pat.2,245,358, 1941 and same 2,306,184, 1943.
23. C. K. Stoddard and E. Pietz, *Bureau of Mines R.I*. 4153, 1947
24. O. Kubaschewski and W. Densch, *J.Inst, Met.*, 1953/54, **82**, 87.
25. Dominion Magnesium Co., Br. Pat. 675,933, 1952, Br. Pat. 664,061, 1952.
26. O. Z. Rylski, *Canad. J. Tech.*, 1954, **32**, 146.
27. L. D. Jaffee and R. K. Piler, *J. Metals*, 1950, **188**, 1396.
28. O. Ruff and F. Neumann, *Z. anorg, Chem*., 1923, **128**, 81.
29. P. Ehrlich and G. Pietzak, *Z. anorg. Chem*., 1954, **275**, 121.
W. Fischer, R. Gewehr and H. Wingchen, *Z. anorg. Chem*, 1939, **242**, 185.
O. Ruff and W. Plato, *Berichte Deutsch Chem, Ges*., 1904, 37, 673.
30. Imperial Chemical Industries, Fr. Pat. 1,069,706, 1954.
31. O. Schmitz, *Z. anorg. Chem.*, 1952, **268**, 61.
32. F. B, Litton and H. C, Anderson, *J. Electrochem, Soc*., 1954, **101**, 287.
33. H. G. Cruickshank, Br. Pat. 675,571, 1952.
34. W. B. Blumenthal, U.S. Pat. 2,550,447, 1951.
LG. Reinert, U.S. Pat. 2,616,784, 1954.
35. W. J. Kroll, *Met, Ind.*, 1952, **80**, 383, 388.
W. J. Kroll, *Metall*., 1955, **9**, 1/2, and continuations.
36. H. Ginsberg, *Z. anorg. Chem*., 1932, **204**, 225.
H. Ginsberg and G. Holder, *Z. anorg. Chem.*, 1931, **201**, 193.
37. F. Haber, *Z, Elektrochemie*, 1902, **8**, 870.
38. Horizons. M. A. Steinberg, M. E. Sibert and E. Wainer, *J. Electrochem. Soc*, 1954, **101**, 63.
39. H. von Wartenberg and O. Fitzner, *Z. anorg. Chem.*, 1926, **151**, 313.
40. H. von Wartenberg, Z. Elektrochemie, 1926, 32, 330.
41. C. B. Gill, M. E. Straumanis and A. W. Schlechten, *J, Electrochem. Soc*., 1955, **102**, 42.
42 L. Andrieux, *Ann, Chim.* 10 ser., 1929, **12**, 421.
43. P. Drossbach, *Z. Elektrochemie*, 1954, **58**, 686.
44. A. J. Kerbecek, Columbia University Diss. Publ. 8254, University Microfilm, Ann Arbor.
45 G. D. P. Cordner and H. W. Worner, *Australian Journ. Applied Science*, 1951, **2**, 358.
46. Shawinigan Water and Power Co., Brit. Pat. 678,807, 1952.
47. Horizons, Brit, Pat. 701,289, 1953.
48. W. J. Kroll, *Trans. Electrochem. Soc.*, 1954, **87**, 551.

49. F. S. Wartman, D.H. Hunter, J. R. Nettle and V. E. Homme, *J. Electrochem. Soc*., 1954, **101**, 507.
50. P. J. Maddox, U.S. Pat. 2,564,337, 1951.
51. D. W. Hardie, *Indus, Chemist*, April, 1954, 161.
52. L. Weiss and E. Neumann, *Z. anorg. Chem.*, 1910, **65**, 262, 328.
L. Weiss and H. Kaiser, *Z, anorg. Chem*., 1910, **65**,388,
53. S. A. Herres and J. A. Davis, *Steel*, 1949, **126**, (18), 82, 135.
H.R. Clauser, *Mat. and Meth.*, 1948, **27** (1), 56.
E. S. Kopecki, *Iron Age*, 1949, **164**, 81.
54. O. Schaber, *Z. Metallkunde*, 1952, **43**, 181.
55. R. M. Parke and J. L. Ham, *Trans A.I.M.E. Metals Div.*, 1947, **171**, 416.
56. W. W. Stephens, H. L. Gilbert and R. A. Beall, Symposium Amer. Soc. Metals, Los Angeles 1953, 111.
57. G. L. Miller, *Indus, Chemist*, 1954, **174**, 577.
58. H. D. Justis and L. Barnett, *Aviation Age*, Sept., 1954, 76.
59. O. W. Simmons, H. R. McCurdy and R. E. Edelman, Trans. Amer Fondrymens Assoc., 1954, **62**, 528.
60. J. M. Blocher and J. F. Campbell, *J. Amer. Chem. Soc*., 1949, 71, 4040.
L. G. Carpenter, *Nature*, 1949, 527.
61. T. R. Magel, P.A. Kulin and A. R. Kaufmann, *J. Metals*, 1952, **4**, 1286.
62. O. W. Simmons and H. R. McCurdy, *Amer, Foundryman*, April, 1953, 121.
63. D. H. Polonis and J.C. Parr, *J. Metals*, 1954, **6,** 1148.
64. *Iron Age*, 1954, **174**, 19.
65. H.B. Bomberger, *Mat. and Meth*., 1954, **40**, 105.
66. G.A. Lenning, C. M, Craighead and R. I. Jaffee, Contract DA-33-019-ORD-938, 1953 and 1954, Battelle Memorial Institute. Summary Reports.
67. A. D. McQuillan, Proc. Royal Soc. London, 1950, A204, 1078.
68. H. H. Hanink, Iron Age, 1952,171, (20),121.
69. J. W. Spretnak and M. G. Fontana, *AF Technical Report* 5662, Wright Dev. Center.
70. W. L. Finlay, J. P. Catlin and J. W. Kaufman, *Steel*, 1955, **136**, (3), 92.
71. L. Luini and E. Lee, *J. Metals*, 1954, **6**, 581.
72. H. W. Worner, *J. Intl. Metals*, 1952, **80**, 213.
M. K. Quillan, *J, Inst. Metals*, 1954,**82**, 433.
73. L. D. Jaffee, *Metal Progress* 1955, **67** (2). 101.
74. Titanium Metals Corporation Handbook on Titanium. 7th Ed. Also Titanium and Titanium Alloys," John L. Everhart, Reinhold Pilot Books, 1954.
75. M. Hansen, D.J. McPherson and W. Rostoker, W.A.D.C Technical Paper, Wright Air Development Center, 1953, 251.
76. W. J. Barth and A. L. Feild, *Metal Progress*, 1953, **64**, 74.
77. F. A. Crossley and H. D. Kessler, *J. Metals*, 1954, **6**, 119.
78. P. Maynard, *Iron Age*, 1954, **173**, 149.
79. J. W. Guliksen, *Iron Age*, 1953, **171**, 136-139.
80. K. A. Wilhelm, *Iron Age*, 1954. **173** (17) and (19), 98, 126.
81. T.E. Perry, *Modern Metals*, October, 1954, 75
82. P. L. Teed, *Engineering*, 1953, **176**, 603. 635
83. W. J. Kroll, *Wiss. Veroeff. aus dem Siemens Konzern*, 1931, X (2), 33.
84. N.F. Mott, Iron Age 1954, **171**, 146.
85. G. T. Bedford, *Mat and Meth*, May. 1952, 99.
86. A.J. Lena, *Iron Age*, 1954, 113.
87. H. S. Brenner, *Modern Metals*, June, 1954, **4**2, 47.
88. *Modern Metals*, January, 1954, 70.